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**Slip-Boundary Equations  
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Nonequilibrium Airflow**

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## Symbols

$A_k^i, B_{k\ell}^i, C_k^{i(j)}$	coefficients of velocity distribution function for $i$ th species
$a_{i0}, a_{i1}, b_{i0}, c_{i0}^{(j)}$	distribution function coefficients given in appendix A and defined in reference 7 for $i$ th species
$a_\infty$	speed of sound, $\sqrt{\gamma RT_\infty}$
$b_0$	distribution function coefficients defined by equation (70c) or (D10)
$C_i$	mass fraction of species $i$
$c_p$	frozen specific heat at constant pressure of mixture, $\sum_i^{\text{NS}} C_i c_{p,i}$
$c_{p,i}$	specific heat at constant pressure of species $i$
$c_v$	frozen specific heat at constant volume
$D_{ij}$	multicomponent diffusion coefficient for species pair $i$ and $j$
$D_i^T$	thermal diffusion coefficient
$\mathcal{D}_{AM}$	binary diffusion coefficient for mixture of atoms and molecules
$\mathcal{D}_{ij}$	binary diffusion coefficient for mixture of species $i$ and $j$
$d_k^j$	diffusion vector of $j$ th species
$E$	total energy flux, $E^T + eM$
$E^T$	energy flux from translational energy
$e$	internal energy that readily equilibrates with translational energy
$F$	general flux of property such as mass, momentum, or energy
$\bar{F}_D$	diffusion coefficient, $\rho \mathcal{D}_{AM} / \mu (U_\infty^2 / c_{p,\infty})$
$f^i$	distribution function of $i$ th species
$f^{(0)i}$	equilibrium (or Maxwellian) distribution function of $i$ th species
$h$	enthalpy of mixture, $\sum_{i=1}^{\text{NS}} C_i h_i$
$h_i$	enthalpy of species $i$ , $\int_{298}^T c_{p,i} dT + \Delta h_{i,298}^f$
$\Delta h_{i,298}^f$	heat of formation for species $i$ at 298°K
$K$	thermal conductivity of mixture
$k$	Boltzmann constant
$k_{wi}$	wall catalytic recombination rate constant for species $i$

$M$	mass flux
$M_\infty$	Mach number, $U_\infty/a_\infty$
$m_i$	mass of $i$ th species
$\bar{m}$	mass of mixture or single-species gas molecule, $(\sum_{i=1}^{NS} \frac{C_i}{m_i})^{-1}$
$N_{Le}$	binary Lewis number, $c_p \rho \mathcal{D}_{AM}/K$
$N_{Le,ij}$	multicomponent Lewis number, $c_p \rho D_{ij}/K$
$N_{Le,ij}$	binary Lewis number, $c_p \rho \mathcal{D}_{ij}/K$
$N_{Pr}$	Prandtl number, $c_p \mu/K$
NS	number of chemical species
$n_i$	number density of species $i$
$n^*$	coordinate measured normal to body in body-filled coordinate system (appendixes C and D)
$\bar{n}$	total number density, $\sum_{i=1}^{NS} n_i$
$P$	momentum flux
$p$	pressure
$p_i$	partial pressure of species $i$
$\dot{q}_w$	wall heat-transfer rate or wall heat flux
$R$	universal gas constant divided by molecular weight of mixture, $\mathcal{R}/\bar{W}$
$\mathcal{R}$	universal gas constant
$R^*$	radius measured from axis of symmetry to point on body surface
$r$	radial distance from body center (appendix E)
$r_N$	body nose radius of curvature (appendix D) or radius of sphere (appendix E)
$s^*$	distance measured along body surface (appendix D)
$T$	temperature
$U_\infty$	free-stream velocity
$u$	velocity component along body surface (appendixes C and D)
$\mathbf{V}$	thermal velocity vector
$V_k^i$	thermal (or peculiar) velocity of $i$ th species (component of $\mathbf{V}$ for species $i$ )
$\bar{V}_k^i$	diffusion velocity
$v_k^i$	total (or molecular) velocity, $v_{0k} + V_k^i$
$v_{0k}$	bulk or mass-averaged velocity

$W_k^i$	nondimensional thermal velocity, $\left(\sqrt{\frac{m_i}{2kT}}\right) V_k^i$
$W_i$	molecular (or atomic) weight of species $i$
$\overline{W}$	molecular weight of mixture
$w_{0k}$	nondimensional mass-averaged velocity $\left(\sqrt{\frac{m_i}{2kT}}\right) v_{0k}$
$x$	coordinate parallel to body (fig. 1)
$y$	coordinate perpendicular to body (fig. 1)
$z$	coordinate parallel to body (fig. 1)
$\alpha$	energy accommodation coefficient
$\beta$	body angle defined in figure D1
$\gamma$	recombination coefficient (or, fraction of incident atoms that recombine at surface)
$\bar{\gamma}$	ratio of frozen specific heats, $c_p/c_v$
$\delta_{kl}$	Kronecker delta
$\varepsilon$	Reynolds number parameter, $(\mu_{\text{ref}}/\rho_{\infty}U_{\infty}r_N)^{1/2}$
$\theta$	accommodation coefficient (or fraction of incident particles that stick)
$\kappa$	surface curvature
$\lambda$	mean free path
$\mu$	viscosity of mixture
$\rho$	density
$\Phi^i(\mathbf{V})$	perturbation part of distribution function
$\phi$	circumferential angle (appendixes D and E)
$\phi^i(\mathbf{V})$	general property of $i$ th species such as mass, momentum, and energy
$\psi_i$	source term defined by equation (38)
Subscripts:	
$A$	atom
$e$	equilibrium value
$k, \ell$	coordinate indices
$M$	molecule
$q$	species index
ref	reference quantity
$x, y, z$	component directions
$y$	normal component
$\parallel, x, z$	tangential components

$\infty$  free-stream value

Superscripts:

$\downarrow$  incident flux

$\uparrow$  specularly reflected flux

Affixes (used both as subscripts and superscripts):

$i, j$  species indices

$s$  edge of Knudsen layer

$w$  wall

A bar over a symbol indicates a dimensionless quantity except for the definitions of  $\bar{v}_k^i$  and  $\bar{V}_k^i$ .

## Summary

Equations are presented for the surface-slip (or jump) values of species concentration, pressure, velocity, and temperature in the low Reynolds number, high-altitude flight regime of a space vehicle. These are obtained from closed-form solutions of the mass, momentum, and energy flux equations by using the Chapman-Enskog velocity distribution function. This function represents a solution of the Boltzmann equation in the Navier-Stokes approximation. The analysis, obtained for nonequilibrium multicomponent airflow, includes the finite-rate surface catalytic recombination and changes in the internal energy during reflection from the surface. Expressions for the various slip quantities have been obtained in a form which can readily be employed in flow-field computations. A consistent set of equations is provided for multicomponent and binary mixtures and single-species gas. An expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture in the absence of slip.

## Introduction

For an accurate prediction of the aerothermal environment of a space vehicle entering the Earth's atmosphere in the low Reynolds number, high-altitude flight regime (ref. 1), the multicomponent, nonequilibrium gas chemistry, as well as the wall slip and catalysis effects, must be evaluated. Such flow fields are of particular interest for aeroassisted orbital transfer and Space Shuttle vehicles. This study was undertaken to obtain the boundary relations that incorporate the effects of slip, multicomponent diffusion, wall catalyticity, and changes in internal energy of the molecules (during reflection from the surface) for application to flow-field calculations under the general assumption of local thermodynamic equilibrium.

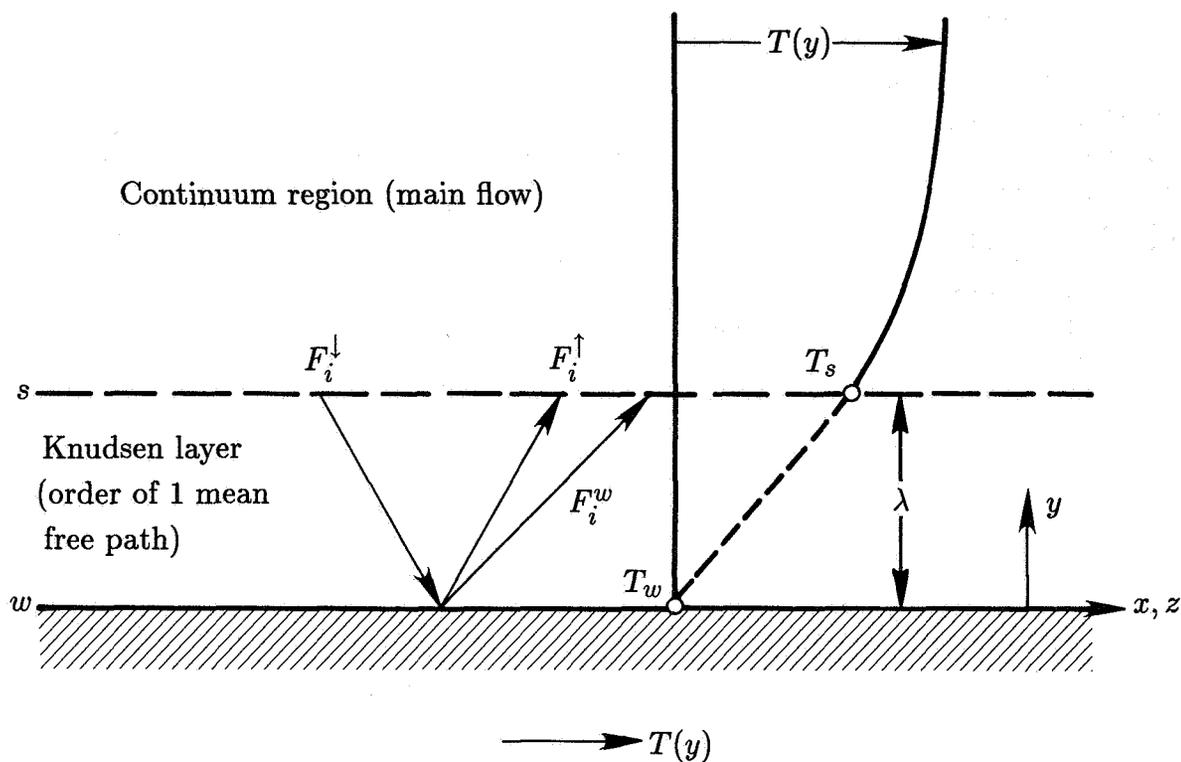
Scott (ref. 2) first presented the wall boundary conditions for a multicomponent mixture with diffusion and wall-catalyzed atom recombination. In obtaining these boundary conditions, he used a first-order velocity distribution function at the edge of the Knudsen layer next to the wall (see fig. 1), where the continuum model of the gas breaks down. These boundary conditions, obtained from the kinetic theory considerations, provide solutions at the top of the Knudsen layer that would match the solution of the Navier-Stokes equations in the bulk outer flow. Hendricks (ref. 3), using Scott's formulation, obtained simplified expressions for engineering applications with some corrections to Scott's expressions. Hendricks' analysis, however, contained some errors in obtaining the engineering expressions. This paper reanalyzes the wall boundary equations by using the approach of reference 2 and provides appropriate relations for the various quantities with surface slip in a form which can readily be employed for flow-field computations. An effort has also been made to reconcile the differences between slip expressions employed by the different researchers. The present analysis provides a consistent formulation for the slip equations for multicomponent and binary mixtures and single-species gas. An expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture (in addition to that for a binary mixture) in the absence of slip. This expression could readily be used in Shuttle-flow-field heating analyses, which include effects of multicomponent diffusion such as reference 4.

The main difference (among other details) between the results contained in reference 5 and the present work is that, in reference 5, the various internal degrees of freedom for a molecule were considered frozen during reflection from the surface whereas they were allowed to change in the present analysis.<sup>1</sup> Further, the results are provided in both spherical and body-oriented coordinate systems.

## Analysis

The slip conditions are taken to exist across the Knudsen layer, which is on the order of one mean free path in thickness as sketched in figure 1. The analysis outlined herein follows the approach of

<sup>1</sup> Since the assumption of local thermodynamic equilibrium is employed, only those internal energies are considered which equilibrate readily with the translational energy.



$F_i^\downarrow$  incident flux;  $F_i^\uparrow$  specularly reflected flux;  $F_i^w$  diffusely reflected flux.

Figure 1. Knudsen layer showing general fluxes and coordinate axes; temperature as function of normal distance is schematically overlaid.

references 2 and 5. It is based on Shidlovskiy's (ref. 6) assumption that the distribution function near the wall can be described to first-order accuracy by the so-called Navier-Stokes approximation. However, a deviation is made from the procedures of Shidlovskiy in that a Chapman-Enskog type distribution function for a multicomponent mixture obtained by the variational method of Hirschfelder, Curtiss, and Bird (ref. 7) is used. The Chapman-Enskog distribution function permits an accurate accounting of diffusion. The analysis contains the following assumptions:

1. The energy and momentum accommodation coefficients (i.e.,  $\alpha$  and  $\theta$ , respectively) have the same value.
2. The fluxes of mass, momentum, and energy across the Knudsen layer are assumed constant. This assumption is consistent with the one of negligible variation of the velocity distribution function through the Knudsen layer.
3. The internal energy associated with the rotational and vibrational modes readily equilibrates with translational energy.

The interaction model at the gas-solid interface, with the various fluxes sketched in figure 1, can be mathematically stated for dissociated air as provided by the following equations.<sup>2</sup>

<sup>2</sup> From the available experimental information, there is no indication that there is significant formation of NO on the Shuttle or other thermal protection surfaces. For this reason, the formation of NO has been neglected in the present model.

For recombining atom:

$$F_A = F_A^\downarrow + (1 - \theta_A)F_A^\uparrow + (\theta_A - \gamma_A)F_A^w \quad (A = O, N) \quad (1)$$

Obviously,

$$\gamma_A \leq \theta_A$$

For molecule gaining from corresponding atom recombination:

$$F_M = F_M^\downarrow + (1 - \theta_M)F_M^\uparrow + \theta_M F_M^w + \gamma_A F_A^w \quad (M = O_2, N_2) \quad (2)$$

For all other atoms and molecules (surface is assumed to be noncatalytic with respect to them):

$$F_i = F_i^\downarrow + (1 - \theta_i)F_i^\uparrow + \theta_i F_i^w \quad (3)$$

where  $F_i$  denotes a convective property such as mass, momentum, or energy.

Summing over all the species gives, from equations (1), (2), and (3), the following expression for the net flux of momentum or energy:

$$\sum_{i=1}^{NS} F_i = \sum_{i=1}^{NS} F_i^\uparrow + \sum_{i=1}^{NS} (1 - \theta_i)F_i^\downarrow + \sum_{i=1}^{NS} \theta_i F_i^w \quad (4)$$

That is, the net flux at the outer edge of the Knudsen layer equals the incident flux, plus the specularly reflected flux (incident minus the fraction that sticks) at the wall, plus the diffusely reflected flux (those that accommodate to the wall) from the wall.

Each species is treated separately in the mass balance equations. Therefore, equation (1), (2), or (3) is employed, depending on the species being considered. In equation (1), the diffusely reflected flux consists of those atoms that are accommodated to the wall minus those that recombine. For the molecules in equation (2), the diffusely reflected term is present along with the source term resulting from the appropriate atoms recombining on the surface.

## Various Fluxes and Distribution Functions

The interaction model of equations (1) through (4) is employed to obtain the slip boundary equations at the gas-solid interface. Through equation (1), the net fluxes of species, momentum, and energy at the outer edge of the Knudsen layer are equated to the difference between the incident and reflected fluxes at the wall. These fluxes are assumed to be constant across the Knudsen layer and are obtained from moments of the distribution function. For a convected property  $\phi^i(\mathbf{V})$  such as mass, momentum, or energy for the  $i$ th species, the net flux of that property normal to the wall at the outer edge of the Knudsen layer, for example, is

$$F_i = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\mathbf{V}) f_s^i(\mathbf{V}) d^3\mathbf{V} \quad (5)$$

where  $v_y^i$  is the normal component of the molecular (or total) velocity and  $f_s^i(\mathbf{V})$  is the velocity distribution function at the edge of the Knudsen layer.

Similar integrals are obtained for the incident and reflected fluxes by integrations over appropriate half-spaces in molecular velocity as shown through the following equations:

Incident flux:

$$F_i^\downarrow = \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} v_y^i \phi^i(\mathbf{V}) f_s^i(\mathbf{V}) d^3\mathbf{V} \quad (6)$$

Specularly reflected flux:

$$F_i^\uparrow = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\mathbf{V}) f_s^i(V_x, -V_y, V_z) d^3\mathbf{V} \quad (7)$$

Diffusely reflected flux:

$$F_i^w = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\mathbf{V}) f_w^i(\mathbf{V}) d^3\mathbf{V} \quad (8)$$

where  $f_w^i$  is the Maxwellian velocity distribution function evaluated at the wall condition and  $V_x$ ,  $V_y$ , and  $V_z$  are the components of the thermal velocity vector  $\mathbf{V}$ . It may be noted that the normal component of the macroscopic (or mass-averaged) velocity  $v_{0y}$  at the surface is zero, so that  $v_y^i = V_y^i$  in equations (5) through (8).

The velocity distribution functions used in integrals contained in relations (5) through (8) are those for a nonuniform multicomponent mixture perturbed out of equilibrium:

$$f^i(\mathbf{V}) = f^{(0)i}(\mathbf{V})[1 + \Phi^i(\mathbf{V})] \quad (9)$$

where  $f^{(0)i}(\mathbf{V})$  is the Maxwellian distribution function for the  $i$ th species given as

$$f^{(0)i}(\mathbf{V}) = \frac{n_i m_i^{3/2}}{(2\pi kT)^{3/2}} \exp\left(-\frac{m_i}{2kT} V_i^2\right) \quad (10)$$

and

$$\Phi^i(\mathbf{V}) = -A_k^i \frac{\partial \ln T}{\partial x_k} - B_{k\ell}^i \frac{\partial v_{0k}}{\partial x_\ell} + \bar{n} \sum_{j=1}^{\text{NS}} C_k^{i(j)} d_k^j \quad (11)$$

Here  $k$  and  $\ell$  are the dummy indices for three coordinate directions, and the summation with index  $j$  represents summation over all the species. The summation convention for repeated indices is used. The coefficients  $A_k^i$ ,  $B_{k\ell}^i$ , and  $C_k^{i(j)}$  are functions of the dimensionless velocity:

$$W_k^i = \sqrt{\frac{m_i}{2kT}} V_k^i \quad (12)$$

and are defined as

$$A_k^i = \left[ a_{i0} + a_{i1} \left( \frac{5}{2} - W_i^2 \right) \right] W_k^i \quad (13)$$

$$B_{k\ell}^i = b_{i0} \left( W_k^i W_\ell^i - \frac{1}{3} W_i^2 \delta_{k\ell} \right) \quad (14)$$

$$C_k^{i(j)} = c_{i0}^{(j)} W_k^i \quad (15)$$

where  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  are constants determined from the variational problem in the first approximation for a mixture as given in reference 7, and  $\delta_{k\ell}$  is the Kronecker delta such that

$$\delta_{k\ell} = 1 \quad (k = \ell)$$

$$\delta_{kl} = 0 \quad (k \neq l)$$

These constants are functions of the collision integrals and are related to the transport properties. The simplified form of these constants is provided in appendix A of this paper. More details can be found in appendix A of reference 2 or in reference 7. The diffusion vector  $d_k^j$  in equation (11) is related to the diffusion velocity of the  $j$ th species and is defined after neglecting the external forces as (ref. 7):

$$d_k^j = \frac{\partial}{\partial x_k} \left( \frac{n_j}{\bar{n}} \right) + \left( \frac{n_j}{\bar{n}} - \frac{n_j m_j}{\rho} \right) \frac{\partial \ln p}{\partial x_k} \quad (16)$$

where  $n_j$  and  $m_j$  are, respectively, the number density and mass of the  $j$ th species;  $\bar{n}$  is the total number density,  $\bar{n} = \sum_j n_j$ ;  $\rho$  is the total mass density,  $\rho = \sum_j n_j m_j$ ; and  $p$  is the total pressure,  $p = \sum_j p_j$ . A simplified form for  $d_k^j$  is provided in appendix A.

The total or mass-averaged velocity  $v_{0k}$  (i.e., the  $k$ th component) appearing in equation (11) is defined as

$$v_{0k} = \frac{1}{\rho} \sum_{j=1}^{\text{NS}} n_j m_j \bar{v}_k^j$$

where  $\bar{v}_k^j$  is the total velocity  $v_k^j$  ( $= v_{0k} + V_k^j$ ) of the  $j$ th species averaged over the distribution function, and  $V_k^j$  is the thermal (or peculiar) velocity, also introduced in equation (5). The thermal velocity  $V_k^j$  of the  $j$ th species averaged over the distribution function is known as the diffusion velocity  $\bar{V}_k^j$ :

$$\bar{V}_k^j = \frac{1}{n_j} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V_k^j f^j(\mathbf{V}) d^3\mathbf{V} \quad (17)$$

A simplified expression for the diffusion velocity in terms of transport properties is provided in appendix A.

## Balance and Slip Equations

Based on equations (1) through (4), the balance equations for the  $i$ th species for fluxes normal to the surface of: (i) the species mass  $M_{iy}$ , (ii) the normal component of momentum  $P_{iy}$ , (iii) the tangential component of momentum  $P_{i\parallel}$ , and (iv) the energy  $E_{iy}$  are obtained as follows:

(i) Species mass flux:

For a recombining atom,

$$M_{Ay} = \theta_A M_A^\downarrow + (\theta_A - \gamma_A) M_A^w \quad (A = \text{O}, \text{N}) \quad (18)$$

For a molecule gaining from the corresponding atom recombination,

$$M_{My} = \theta_M M_M^\downarrow + \theta_M M_M^w + \gamma_A M_A^w \quad (M = \text{O}_2, \text{N}_2) \quad (19)$$

For all other atoms and molecules,

$$M_{iy} = \theta_i M_i^\downarrow + \theta_i M_i^w \quad (20)$$

(ii) Normal momentum flux:

$$\sum_{i=1}^{\text{NS}} P_{iy} = \sum_{i=1}^{\text{NS}} (2 - \theta_i) P_i^\downarrow + \sum_{i=1}^{\text{NS}} \theta_i P_i^w = P_y \quad (21)$$

(iii) Tangential momentum flux:

$$\sum_{i=1}^{\text{NS}} P_{i\parallel} = \sum_{i=1}^{\text{NS}} \theta_i P_i^\downarrow \quad (22)$$

(iv) Energy flux:<sup>3</sup>

$$\begin{aligned} E_y &= \sum_{i=1}^{\text{NS}} E_{iy} = \sum_{i=1}^{\text{NS}} E_{iy}^T + \sum_i^{\text{Diatomic molecules}} e_{iy} M_{iy} \\ &= \sum_{i=1}^{\text{NS}} \theta_i E_i^{T\downarrow} + \sum_{i=1}^{\text{NS}} \theta_i E_i^{T,w} + \sum_i^{\text{Diatomic molecules}} \theta_i e_i^s M_i^\downarrow \\ &\quad + \sum_i^{\text{Diatomic molecules}} \theta_i e_i^w M_i^w \end{aligned} \quad (23)$$

where  $e_i$  is the internal energy of  $i$ th species that readily equilibrates with the translational energy  $E_i^T$  under the assumption of local thermodynamic equilibrium. For example,

$$e_i^{\text{rotation}} = \frac{kT}{m_i}$$

Further, in writing the energy flux balance of equation (23) it has been assumed that there is no change in internal energy during specular reflection.

In obtaining equations (18) through (23) we have used the following relations:

$$\begin{aligned} M_i^\uparrow &= -M_i^\downarrow & P_{i\parallel}^\uparrow &= -P_{i\parallel}^\downarrow \\ E_i^\uparrow &= -E_i^\downarrow & P_{i\parallel}^w &= 0 & P_{iy}^\downarrow &= P_{iy}^\uparrow \end{aligned}$$

Because it is assumed that the atoms are consumed at the wall by catalytic recombination in equation (18), the net mass flux is not equal to zero,  $M_{Ay} \neq 0$ . Similarly, the net mass flux is not equal to zero,  $M_{My} \neq 0$ , in equation (19). However,  $M_{iy} = 0$ , is equal to zero, in equation (20) for the atoms and molecules for whom the surface is assumed noncatalytic.

Substituting equations (5), (6), (7), and (8) with the definition of  $\phi^i(\mathbf{V})$  as mass for equations (18) through (20), as normal component of momentum for equation (21), as tangential component of momentum for equation (22), and as energy for equation (23), respectively, and carrying out the

<sup>3</sup> The energy balance is based on the assumption that the various energies considered readily equilibrate with the translational energy.

integrations<sup>4</sup> gives equations relating the slip properties to wall properties and gradients at the edge of Knudsen layer. All accommodation coefficients  $\theta_i$  are assumed to be equal to  $\theta$ .

Concentration (number density) slip (obtained from mass flux balance):

$$\frac{n_i^s}{n_i^w} = 2 \left( 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right) \sqrt{\frac{T_w}{T_s}} / \left( \frac{P_{iy}}{p_i^s} + 1 \right) \quad (24)$$

where  $M_{iy}$  and  $P_{iy}/p_i^s$  are given by equations (B1) and (B17), respectively. Alternatively, a more simplified expression for  $M_{iy}$  may be obtained from equations (34) and (35).

Pressure slip (obtained from the flux balance of normal component of momentum):

$$p_s = \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{2-\theta}{\sqrt{\pi}} \left[ k \frac{\partial T}{\partial y} \sum_{i=1}^{\text{NS}} n_i \left( a_{i0} - \frac{1}{2} a_{i1} \right) \right]_s + \frac{\theta}{2} p^w \right\} / \left[ \frac{\theta}{2} + \frac{2-\theta}{\sqrt{\pi}} \sum_i \left( n_i \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_y^j \right) \right]_s \quad (25)$$

with viscosity

$$\mu = \frac{1}{2} kT \sum_{i=1}^{\text{NS}} n_i b_{i0}$$

Velocity slip (obtained from the flux balance of tangential component of momentum):

$$v_{0x}^s = \left\{ \sqrt{\pi} \frac{2-\theta}{2\theta} \mu_s \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right)_s + \frac{1}{2} \sum_{i=1}^{\text{NS}} p_i^s \left[ \frac{\partial \ln T}{\partial x} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \bar{n} \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_x^j \right]_s \right\} / \sum_{i=1}^{\text{NS}} p_i^s \sqrt{\frac{m_i}{2kT_s}} \quad (26)$$

$$v_{0z}^s = \left\{ \sqrt{\pi} \frac{2-\theta}{2\theta} \mu_s \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right)_s + \frac{1}{2} \sum_{i=1}^{\text{NS}} p_i^s \left[ \frac{\partial \ln T}{\partial z} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \bar{n} \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_z^j \right]_s \right\} / \sum_{i=1}^{\text{NS}} p_i^s \sqrt{\frac{m_i}{2kT_s}} \quad (27)$$

<sup>4</sup> The mass, momentum, and energy fluxes in terms of evaluated integrals over the distribution function are given in appendix B.

Temperature slip:

$$(2kT_s)^{3/2} = \left[ -2\sqrt{\pi} \frac{2-\theta}{2\theta} \sum_{i=1}^{NS} E_{iy} + (2kT_w)^{3/2} \sum_{i=1}^{NS} \frac{n_i^w}{\sqrt{m_i}} \right] / \sum_{i=1}^{NS} \frac{n_i^s}{\sqrt{m_i}} \times \left[ 1 + \frac{1}{4} b_{i0} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right] \quad (28)$$

Equations (24) through (28) differ from the corresponding expressions provided in reference 2 because of the differences in the interaction model employed at the gas-solid interface and typographical errors.

The constants  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  (also known as the Sonine expansion coefficients) appearing in equations (24) through (28) may now be expressed in terms of the transport properties as given in appendix A. By using these relations along with the various flux expressions of appendix B and also expressing  $d_k^j$  in terms of the gradient of mass fractions  $\partial C_j / \partial y$  as given in appendix A (by neglecting diffusion due to pressure gradients and external forces), the following equations are obtained after some algebraic simplifications:<sup>5</sup>

Concentration (number density) slip:

Please note that the following equation is the same as equation (24) and is unchanged:

$$\frac{n_i^s}{n_i^w} = 2 \left( 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right) \sqrt{\frac{T_w}{T_s}} / \left( \frac{P_{iy}}{p_i^s} + 1 \right)$$

Pressure slip:

$$p^s = \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{2}{5} \frac{(2-\theta)}{\sqrt{\pi}} \left( \frac{1}{\bar{n}} \frac{\partial T}{\partial y} \sum_{i=1}^{NS} n_i K_i \sqrt{\frac{m_i}{2kT}} \right)_s + \frac{\theta}{2} p^w \right\} / \left[ \frac{\theta}{2} + 2 \frac{(2-\theta)}{\sqrt{\pi}} \sum_{i=1}^{NS} \sqrt{\frac{m_i}{2kT_s}} \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left( \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s \right] \quad (29)$$

Velocity Slip:

$$v_{0x}^s = \left\{ \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s + \frac{1}{5} \left( \frac{1}{\bar{n}kT} \frac{\partial T}{\partial x} \sum_{i=1}^{NS} n_i \sqrt{m_i} K_i \right)_s - \bar{n}_s \sum_{i=1}^{NS} \sqrt{m_i} \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left( \frac{\partial C_j}{\partial x} - C_j \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial x} \right)_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (30)$$

<sup>5</sup> The approximations made in the expressions for  $a_{i1}$  and  $b_{i0}$  are given in appendix A.

$$v_{0z}^s = \left\{ \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s + \frac{1}{5} \left( \frac{1}{\bar{n}kT} \frac{\partial T}{\partial z} \sum_{j=1}^{NS} n_j \sqrt{m_j} K_j \right)_s \right. \\ \left. - \bar{n}_s \sum_{i=1}^{NS} \sqrt{m_i} \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left( \frac{\partial C_j}{\partial z} - C_j \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial z} \right)_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (31)$$

Temperature slip:

$$\frac{T_s}{T_w} = \left[ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{2\bar{n}_s} \sum_i \frac{m_i e_i^w M_{iy}}{kT_w m_i} - \frac{\sqrt{\pi}}{2\bar{n}_s} \frac{2 - \theta}{\theta} \sum_i \frac{m_i e_i^s M_{iy}}{kT_w m_i} \right. \\ \left. + \frac{1}{4} \sum_i \sqrt{\frac{2kT_s \bar{m}_s}{m_i}} \frac{C_i^s (e_i^w - e_i^s) m_i}{m_i kT_w} \left( \frac{P_{iy}}{p_i^s} + 1 \right) + \frac{1}{2} \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \left( \frac{P_{iy}}{p_i^s} + 1 \right) \right] \\ / \left[ -\sqrt{\pi} \frac{2 - \theta}{\theta} \left( \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \frac{M_{iy}}{\bar{n} m_i} \right)_s + \frac{1}{4} \sum_{i=1}^{NS} \sqrt{\frac{2kT_s \bar{m}_s}{m_i}} C_i^s \left( 3 \frac{P_{iy}}{p_i^s} + 1 \right) \right] \quad (32)$$

where the mass fraction  $C_i$  and the mass of a mixture molecule  $\bar{m}$  are defined, respectively, as

$$C_i = \frac{n_i m_i}{\rho}$$

and

$$\bar{m} = \left( \sum_{j=1}^{NS} \frac{C_j}{m_j} \right)^{-1}$$

Equations (24), (29), (30), (31), and (32) differ from equations (23) and (25) through (28) of reference 3. For dissociated air, the gas-surface interaction model employed in reference 3 appears to be inconsistent. Further, the diffusion vector  $d_k^j$  appears to have been incorrectly evaluated in reference 3. If one carries out the simplifications in equations (23), (24), and (28) of reference 3 (which contain the binary assumption) through the evaluation of  $\frac{\partial}{\partial y} \left( \frac{n_j}{\bar{n}} \right)$  in terms of mass fraction as given by equations (35), (36), and (39) of the same reference, erroneous results are obviously obtained because  $\sum_{j=1}^{NS} \left( \frac{\partial C_j}{\partial r} \right)_s$  (which is zero by definition) is contained as a factor in several of these equations.

For the first-order recombination at the surface, the following relation between the atom mass flux  $M_{Ay}$  and the wall number density  $n_A^w$  may be employed:

$$M_{Ay} = -k_{wA}n_A^w m_A \quad (33)$$

where the minus sign indicates that the flux is in the direction opposite to the outward normal, and the expression for the rate constant  $k_{wA}$  with diffusion and slip is (ref. 2)<sup>6</sup> as follows:

$$k_{wA} = \gamma_A \sqrt{\frac{kT_w}{2\pi m_A}} \quad (34)$$

Here  $\gamma_A$  is the recombination coefficient.

For a fully catalytic wall ( $\gamma_A = 1$ ), the maximum value of the rate constant  $k_{wA}$  is limited by the surface temperature. The reaction rate constant for a fully catalytic wall with the gas phase in chemical equilibrium is often assumed to be infinity for the sake of simplicity.

If equation (33) is employed, the net mass flux  $M_{iy}$  appearing in equations (24) and (32) may be obtained from

$$M_{Ay} = -k_{wA}n_A^w m_A \quad (A = O, N) \quad (35a)$$

$$M_{My} = k_{wA}n_A^w m_A \quad \left( \begin{array}{l} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{array} \right) \quad (35b)$$

$$M_{iy} = 0 \quad (\text{For all other atoms and molecules}) \quad (35c)$$

Equation (24), with  $M_{iy}$  defined by equations (35), gives the number density ratio  $n_i^s/n_i^w$ . However, to obtain  $n_i^w$  from this ratio, an expression for  $n_i^s$  is required.

The net mass flux of O and N atoms to the surface,  $M_{Ay}$ , is also equal to the rate of consumption of these atoms at the wall from surface recombination:

$$M_{Ay} = \gamma_A M_{Ay}^\downarrow \quad (A = O, N) \quad (36a)$$

and the corresponding net mass flux of O<sub>2</sub> and N<sub>2</sub> molecules will be

$$M_{My} = -\gamma_A M_{My}^\downarrow \quad \left( \begin{array}{l} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{array} \right) \quad (36b)$$

For all other species, the net mass flux to the surface may be assumed to be zero. Thus,

$$M_{iy} = 0 \quad (36c)$$

<sup>6</sup> As shown in reference 2, by neglecting slip but keeping diffusion, a slightly different form of equation (34) is obtained:

$$k_{wA} = \frac{2\gamma_A}{2 - \gamma_A} \sqrt{\frac{kT_w}{2\pi m_A}}$$

Substitution of the net and incident fluxes  $M_{ij}$  and  $M_i^{\downarrow}$  from equations (B1) and (B2), respectively, into equation (36) gives the following expression (after thermal diffusion is neglected):

$$\sum_{\substack{j=1 \\ j \neq i}}^{\text{NS}} D_{ij}^s \left( \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{\text{NS}} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s = \frac{\psi_i^s}{m_i} \quad (37)$$

which may be used to obtain  $n_i^s$ .<sup>7</sup> Here  $\psi_i^s$  is the source term defined as

$$\psi_A^s = -\frac{\gamma_A}{(2-\gamma_A)} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^s}{2\bar{n}_s} \sqrt{\frac{2kT_s}{m_A}} \left( \frac{P_{Ay}}{p_A^s} + 1 \right) \quad (38a)$$

For O<sub>2</sub> and N<sub>2</sub> molecules

$$\psi_M^s = -\psi_A^s \quad \begin{cases} A = \text{O for } M = \text{O}_2 \\ A = \text{N for } M = \text{N}_2 \end{cases} \quad (38b)$$

For all other species

$$\psi_i^s = 0 \quad (38c)$$

## Simplifications for Multicomponent Mixture

Equations (24) and (29) through (32) for multicomponent gas flows can be simplified if one makes the following assumptions:

1. All diffusion coefficients  $D_{ij}$  for a multicomponent gas have the same value so that  $D_{ij} = D_{AM}$ ,<sup>8</sup>  $D_{AM}$  is the same as the binary diffusion coefficient  $\mathcal{D}_{AM}$ .

<sup>7</sup> If no assumption is made about  $D_{ij}$ , equation (37) would give the following expression for  $(\partial C_i / \partial y)_s$  for all the species:

$$\left( \frac{\partial C_i}{\partial y} \right)_s = \frac{m_i}{\bar{m}_s} \left[ \sum_{\substack{j=1 \\ j \neq i}}^{\text{NS}} D_{ij}^s \left( \frac{\partial C_j}{\partial y} - C_j \sum_{\substack{q=1 \\ q \neq i}}^{\text{NS}} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s - \frac{\psi_i}{m_i} \right] / \sum_{\substack{j=1 \\ j \neq i}}^{\text{NS}} (D_{ij} C_j)_s$$

The source term  $\psi_i$  in this expression, however, may be simplified to yield the following expression for  $C_A^s$  (or  $n_A^s$ ) for the *recombining atoms only*:

$$C_A^s = \frac{m_A n_A^s}{\rho_s} = -2\sqrt{\pi} \frac{2-\gamma_A}{\gamma_A} \frac{m_A}{\bar{m}_s} \sqrt{\frac{m_A}{2kT_s}} \sum_{\substack{j=1 \\ j \neq A}}^{\text{NS}} D_{Aj}^s \left( \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{\text{NS}} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s / \left( \frac{P_{Ay}}{p_A^s} + 1 \right)$$

<sup>8</sup> This is a somewhat stronger assumption because  $D_{ij}$  is concentration dependent, whereas  $\mathcal{D}_{ij}$  is virtually independent of composition. The multicomponent diffusion coefficient  $D_{ij}$  is related to the binary diffusion coefficient  $\mathcal{D}_{ij}$  through the following relations (ref. 7):

$$D_{ij} = \bar{K}_{ij} - (M_i/M_j) \bar{K}_{ii}$$

where quantities  $\bar{K}_{ij}$  are coefficients in a matrix which is the inverse of the matrix with the following coefficients:

$$K_{ij} = \frac{C_i}{\mathcal{D}_{ij}} + M_j \sum_{\substack{q=1 \\ q \neq i}}^{\text{NS}} \frac{C_q}{M_q \mathcal{D}_{iq}} \quad (i \neq j)$$

$$= 0 \quad (i = j)$$

One can see, therefore, that by employing  $D_{AM}$  (which is the same as  $\mathcal{D}_{AM}$ ) for all the species in a multicomponent gas mixture, considerable saving is obtained in computational effort and time without losing the general flavor of multicomponent diffusion. This is particularly true if the dissociated air consists predominantly of nitrogen molecules and oxygen atoms. The Shuttle entry conditions fall into this category. Simple and multicomponent diffusion gave the same results in reference 8.

2. The ratio of normal momentum flux to the pressure  $P_{iy}/p_i$  is the same for all species and equal to that of the mixture; this also implies that the normal shear stress  $\tau_{yyi}$  for species  $i$  is the same as that for the mixture  $\tau_{yy}$ .
3. The rotational and vibrational states are fully excited so that the internal energy  $e_i$  for the diatomic molecules in air may be taken as equal to  $2kT/m_i$  at the edge of Knudsen layer. Implicit here is the assumption that excitation of the electronic states of the atoms and molecules does not contribute to the internal energy of the particle. This will be true for a relatively cold surface.

These assumptions retain the major effects of multicomponent fluxes on various slip quantities and provide considerable saving in the computational effort required for the analysis of a flow problem (refs. 2 and 8). With these simplifications, equations (24) and (29) through (32) yield the following results:

Concentration slip:

$$\frac{n_i^s}{n_i^w} = 2 \left( 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right) \sqrt{\frac{T_w}{T_s}} / \left( \frac{P_y}{p^s} + 1 \right) \quad (39)$$

where  $M_{iy}$  may be obtained from equations (35) and  $P_y/p^s$  is given by equation (B17) with the simplifications mentioned earlier in this section.

Pressure slip:

$$\begin{aligned} \frac{p^s}{p^w} = & \left\{ \frac{\theta}{2} - \frac{\theta}{3\bar{n}_w kT_w} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{2(2-\theta)}{5} \frac{1}{\sqrt{\pi}} \frac{1}{\bar{n}_w kT_w} \right. \\ & \times \left. \left( \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial y} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right)_s \right\} / \left\{ \frac{\theta}{2} - \frac{2(2-\theta)}{\sqrt{\pi}} \frac{\mathcal{D}_{AM}^s}{\sqrt{2kT_s}} \sum_{i=1}^{NS} \sqrt{m_i} \right. \\ & \times \left. \left[ \frac{\partial C_i}{\partial y} + (1 - C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right]_s \right\} \quad (40) \end{aligned}$$

Velocity slip:

$$\begin{aligned} v_{0x}^s = & \left\{ \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s + \frac{1}{5} \left( \frac{1}{kT} \frac{\partial T}{\partial x} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right)_s \right. \\ & \left. + \bar{n}_s \mathcal{D}_{AM}^s \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial x} + (1 - C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial x} \right]_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (41) \end{aligned}$$

$$\begin{aligned} v_{0z}^s = & \left\{ \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s + \frac{1}{5} \left( \frac{1}{kT} \frac{\partial T}{\partial z} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right)_s \right. \\ & \left. + \bar{n}_s \mathcal{D}_{AM}^s \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial z} + (1 - C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial z} \right]_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (42) \end{aligned}$$

Temperature slip:

$$\begin{aligned}
\frac{T_s}{T_w} = & \left[ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_i \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_i \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s \right. \\
& \left. + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s \right] / \left[ -\sqrt{\pi} \frac{2-\theta}{\theta} \left( \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \frac{M_{iy}}{\bar{n} m_i} - \frac{1}{\bar{n}} \sum_i \frac{M_{iy}}{m_i} \right) \right. \\
& \left. + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_i \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s \right] \quad (43a)
\end{aligned}$$

or, if the internal energy is frozen during reflection from the surface (see eq. (28) of ref. 5, for example),

$$\begin{aligned}
\frac{T_s}{T_w} = & \left[ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s \right] / \left[ -\sqrt{\pi} \frac{2-\theta}{\theta} \left( \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \frac{M_{iy}}{\bar{n} m_i} \right) \right. \\
& \left. + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s \bar{m}_s}{m_i m_i}} C_i^s \right] \quad (43b)
\end{aligned}$$

Equation (37) may also be simplified to yield an explicit expression for  $n_i^s$ :

$$n_i^s = \frac{\rho_s}{m_i} \left\{ 1 + \frac{1}{\bar{m}} \left[ \left( \frac{\partial C_i}{\partial y} \right)_s + \frac{1}{m_i} \left( \frac{\psi_i}{\mathcal{D}_{AM}} \right)_s \right] / \sum_{q=1}^{NS} \left( \frac{1}{m_q} \frac{\partial C_q}{\partial y} \right)_s \right\} \quad (44)$$

where

$$\psi_A^s = -\frac{\gamma_A}{2-\gamma_A} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^s}{2\bar{n}_s} \sqrt{\frac{2kT_s}{m_A}} \left( \frac{P_{Ay}}{p_A^s} + 1 \right) \quad (A = O, N) \quad (45a)$$

$$\psi_M^s = -\psi_A^s \quad \left( \begin{array}{l} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{array} \right) \quad (45b)$$

$$\psi_i^s = 0 \quad (\text{For all other species}) \quad (45c)$$

It is suggested here that the concentration for the major species (for example, nitrogen) be obtained by requiring the sum of concentrations of all the species to equal unity. It should be mentioned that the mass of the  $i$ th species  $m_i$  is related to the molecular (or atomic) weight  $W_i$  through the relation

$$\frac{m_i}{W_i} = \frac{k}{\mathcal{R}} \quad (46)$$

where  $k$  is the Boltzmann constant and  $\mathcal{R}$  is the universal gas constant.

## Concentration Slip Boundary Condition for Fully Catalytic or Noncatalytic Surface

Equation (44) gives slip values of the concentration  $n_i^s$  for a finite catalytic surface. For a fully catalytic ( $\gamma_A = 1$ ) surface, one generally assumes complete recombination of atoms at the surface. There is a discrepancy in this assumption because the maximum recombination rate is limited by the surface temperature as discussed earlier. (See the discussion following equation (34).) Thus, for a fully catalytic surface, equation (44) should be employed with  $\gamma_A = 1$ .

For a noncatalytic surface ( $\gamma_A = 0$ ), equations (45) give  $\psi_i^s = 0$  for all the species. Then equation (44) becomes

$$n_i^s = \frac{\rho_s}{m_i} \left\{ 1 + \left[ \left( \frac{\partial C_i}{\partial y} \right)_s / \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s \right] \right\} \quad (47a)$$

which may also be written as

$$\left( \frac{\partial C_i}{\partial y} \right)_s = -(1 - C_i^s) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s \quad (47b)$$

Summing the above equation over all the species gives

$$\sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s = 0 \quad (48)$$

for a noncatalytic surface. Therefore, equation (47a) is not an appropriate boundary condition. However, employing equation (48) with equation (47b) yields

$$\left( \frac{\partial C_i}{\partial y} \right)_s = 0 \quad (49)$$

which may be used as the boundary condition for a noncatalytic surface with a multicomponent gas mixture.

## Simplifications for Binary Mixture

At lower altitudes (i.e., when the Reynolds number parameter  $\varepsilon^2$  of reference 9 is much less than 1) with the flow in slight nonequilibrium, the derivatives of various quantities with respect to  $x$  and  $z$  and some other higher order terms like  $\partial v_{0y}/\partial y$  may be dropped through an order of magnitude analysis. (See ref. 10, for example.) Further, the dissociated air may be considered as a binary mixture (i.e., consisting of atoms and molecules only, see ref. 9) at these altitudes. If an assumption is also made that the internal energy of the molecules remains frozen during reflection from the surface, equations (39) through (44) can be simplified further to the following forms.

Concentration slip:

$$\frac{n_A^s}{n_A^w} = \frac{2 - \gamma_A}{2} \sqrt{\frac{T_w}{T_s}} \quad (50)$$

Pressure slip:

$$\frac{p^s}{p^w} = \left[ 1 + \frac{4}{5\sqrt{\pi}} \frac{2 - \theta}{\theta} \frac{1}{\bar{n}_w k T_w} \left( \frac{\bar{m}}{\sqrt{2kT}} \frac{\partial T}{\partial y} \right)_s \left( \frac{C_A^s K_A}{\sqrt{m_A}} + \frac{1 - C_A^s}{\sqrt{m_M}} K_M \right) \right] / \left[ 1 - \frac{4}{\sqrt{\pi}} \frac{2 - \theta}{\theta} \frac{D_{AM}^s}{\sqrt{2kT_s}} \right. \\ \left. \times \frac{\bar{m}_s \sqrt{m_M} - \sqrt{m_A}}{\sqrt{m_A m_M}} \left( \frac{\partial C_A}{\partial y} \right)_s \right] \quad (51)$$

Velocity slip:

$$v_{0x}^s = \left[ \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} \left( \frac{\mu}{\sqrt{\kappa T}} \frac{\partial v_{0x}}{\partial y} \right)_s \right] / \left[ (\sqrt{m_A} - \sqrt{m_M}) n_A^s + \bar{n}_s \sqrt{m_M} \right] \quad (52)$$

$$v_{0z}^s = \left[ \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} \left( \frac{\mu}{\sqrt{\kappa T}} \frac{\partial v_{0z}}{\partial y} \right)_s \right] / \left[ (\sqrt{m_A} - \sqrt{m_M}) n_A^s + \bar{n}_s \sqrt{m_M} \right] \quad (53)$$

Temperature slip:

$$\begin{aligned} \frac{T_s}{T_w} &= \left( \sqrt{\frac{2\kappa T_s}{m_A}} \frac{\bar{m}_s}{m_A} \left\{ \left[ 1 - 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right] C_A^s + 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right\} + \sqrt{\frac{2\kappa T_w}{m_A}} \frac{\gamma_A n_A^w}{2\bar{n}_s} \right. \\ &\times \left. \left( 1 - 2 \frac{m_A}{m_M} \right) \right) / \left( -\sqrt{\pi} \frac{2 - \theta}{\theta} \left[ \frac{1}{2} \left( \frac{K}{p} \frac{\partial T}{\partial y} \right)_s + \frac{1}{4\sqrt{\pi}} \left( 5 - 9 \frac{m_A}{m_M} \right) \sqrt{\frac{2\kappa T_w}{m_A}} \frac{\gamma_A n_A^w}{2\bar{n}_s} \right] \right. \\ &\left. + \sqrt{\frac{2\kappa T_s}{m_A}} \frac{\bar{m}_s}{m_A} \left\{ \left[ 1 - 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right] C_A^s + 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right\} \right) \end{aligned} \quad (54a)$$

or, with frozen internal energy during surface reflection,

$$\begin{aligned} \frac{T_s}{T_w} &= \left( \sqrt{\frac{2\kappa T_s}{m_A}} \frac{\bar{m}_s}{m_A} \left\{ \left[ 1 - \left( \frac{m_A}{m_M} \right)^{3/2} \right] C_A^s + \left( \frac{m_A}{m_M} \right)^{3/2} \right\} + \sqrt{\frac{2\kappa T_w}{m_A}} \frac{\gamma_A n_A^w}{2\bar{n}_s} \right. \\ &\times \left. \left( 1 - \frac{m_A}{m_M} \right) \right) / \left( -\sqrt{\pi} \frac{2 - \theta}{\theta} \left[ \frac{1}{2} \left( \frac{K}{p} \frac{\partial T}{\partial y} \right)_s + \frac{5}{4\sqrt{\pi}} \left( 1 - \frac{m_A}{m_M} \right) \sqrt{\frac{2\kappa T_w}{m_A}} \frac{\gamma_A n_A^w}{2\bar{n}_s} \right] \right. \\ &\left. + \sqrt{\frac{2\kappa T_s}{m_A}} \frac{\bar{m}_s}{m_A} \left\{ \left[ 1 - \left( \frac{m_A}{m_M} \right)^{3/2} \right] C_A^s + \left( \frac{m_A}{m_M} \right)^{3/2} \right\} \right) \end{aligned} \quad (54b)$$

In equations (54),  $n_A^w$  is obtained from  $n_A^s$  by using equation (50).

Expression for  $n_A^s$ :

$$\begin{aligned} n_A^s &= \frac{\rho_s}{m_A} \left[ \left( \frac{1}{\bar{m}} + \frac{1}{m_A} - \frac{1}{m_M} \right) \frac{\partial C_A}{\partial y} - \frac{2\gamma_A}{2 - \gamma_A} \sqrt{\frac{\kappa T}{2\pi m_A}} \frac{n_A}{\rho \mathcal{D}_{AM}} \right]_s \\ &/ \left( \frac{1}{m_A} - \frac{1}{m_M} \right) \left( \frac{\partial C_A}{\partial y} \right)_s \end{aligned} \quad (55a)$$

which may also be written as

$$\frac{n_A^s m_A}{\rho_s} = C_A^s = \frac{2 - \gamma_A}{2\gamma_A} \sqrt{\frac{2\pi m_A}{\kappa T_s}} \mathcal{D}_{AM}^s \left( \frac{\partial C_A}{\partial y} \right)_s \quad (55b)$$

For a fully catalytic surface ( $\gamma_A = 1$ ), equation (55b) gives appropriate value for the concentration slip.<sup>9</sup> The relevant boundary condition for a noncatalytic surface ( $\gamma_A = 0$ ) is

$$\left(\frac{\partial C_A}{\partial y}\right)_s = 0 \quad (56)$$

as can readily be seen from equation (55b).

### Comparison With Existing Expressions

For a noncatalytic surface ( $\gamma_A = 0$ ), pressure and temperature slip equations (51) and (54b) are further simplified, with the help of equation (56), to the following equations:

Pressure slip:

$$p^s = p^w + \frac{4}{5\sqrt{\pi}} \frac{2 - \theta}{\theta} \left(\frac{\bar{m}}{\sqrt{2kT}} \frac{\partial T}{\partial y}\right)_s \left(\frac{C_A^s K_A}{\sqrt{m_A}} + \frac{1 - C_A^s}{\sqrt{m_M}} K_M\right) \quad (57)$$

Temperature slip (with frozen internal energy during reflection from the surface):

$$T_s = T_w + \sqrt{\pi} \frac{2 - \theta}{2\theta} \left(\frac{K}{k} \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial y}\right)_s \left/ \left\{ \bar{m}_s \bar{n}_s \left[ \left(\frac{1}{m_A^{3/2}} - \frac{1}{m_M^{3/2}}\right) C_A^s + \frac{1}{m_M^{3/2}} \right] \right\} \right. \quad (58)$$

Equations (52), (53), (57), and (58) (with the noncatalytic surface assumption in equations (57) and (58)) can be rewritten as

Velocity slip:

$$v_{0x}^s = A_1 a_1 \frac{1}{\bar{n}_s \sqrt{\bar{m}_s}} \left(\frac{\mu}{\sqrt{kT}} \frac{\partial v_{0x}}{\partial y}\right)_s \quad (59)$$

$$v_{0z}^s = A_1 a_1 \frac{1}{\bar{n}_s \sqrt{\bar{m}_s}} \left(\frac{\mu}{\sqrt{kT}} \frac{\partial v_{0z}}{\partial y}\right)_s \quad (60)$$

Pressure slip:

$$p^s = p^w + B_1 b_1 \left(\frac{\bar{\gamma} - 1}{\bar{\gamma}}\right)_s \left(\sqrt{\frac{\bar{m}}{kT}} K \frac{\partial T}{\partial y}\right)_s \quad (61)$$

Temperature slip:

$$T_s = T_w + C_1 c_1 \left(\frac{\bar{\gamma} - 1}{\bar{\gamma}}\right)_s \left(\frac{K}{k} \frac{1}{\sqrt{kT}} \frac{\partial T}{\partial y} \left/ \frac{\bar{n}}{\sqrt{\bar{m}}}\right.\right)_s \quad (62)$$

<sup>9</sup> Sometimes in the literature  $C_A$  is prescribed as zero for a fully catalytic surface. Strictly speaking, this is true only when the Reynolds number parameter  $\varepsilon^2$  (ref. 9) is approximately zero (close to the chemical equilibrium condition at low altitudes) and the surface is highly cooled. This can easily be seen by nondimensionalizing equation (55b) in a way similar to equation (2.8d) of reference 9. Thus, the recombination rate coefficient  $\gamma_A$  and density (as measured through  $\varepsilon^2$ ) both control the recombination rate and not  $\gamma_A$  alone.

where

$$\begin{aligned}
A_1 &= \frac{\bar{n}_s \sqrt{\bar{m}_s}}{(\sqrt{m_A} - \sqrt{m_M}) n_A^s + \sqrt{m_M} \bar{n}_s} \frac{16}{5\pi} \\
B_1 &= \left( \sqrt{\frac{m_A}{\bar{m}}} \frac{C_A K_A}{m_A} + \sqrt{\frac{m_M}{\bar{m}}} \frac{C_M K_M}{m_M} \right)_s \frac{64}{75\pi} \frac{\bar{\gamma}}{\bar{\gamma} - 1} \bigg/ \left( \frac{C_A K_A}{m_A} + \frac{C_M K_M}{m_M} \right)_s \\
C_1 &= \left\{ \bar{m}^{3/2} \left[ \left( \frac{1}{m_A^{3/2}} - \frac{1}{m_M^{3/2}} \right) C_A + \frac{1}{m_M^{3/2}} \right] \right\}^{-1} \frac{128}{150\pi} \frac{\bar{\gamma}}{\bar{\gamma} - 1} \\
a_1 &= \frac{5\pi}{16} \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} = 1.2304 \frac{2 - \theta}{\theta} \\
b_1 &= \frac{15}{16} \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} = 1.1750 \frac{2 - \theta}{\theta} \\
c_1 &= \frac{75\pi}{128} \sqrt{\frac{\pi}{2}} \frac{2 - \theta}{\theta} = 2.3071 \frac{2 - \theta}{\theta}
\end{aligned}$$

The concentration slip condition consistent with equations (59), (60), (61), and (62) is

$$\left( \frac{\partial C_A}{\partial y} \right)_s = 0 \quad (63)$$

The range of values of  $A_1$ ,  $B_1$ , and  $C_1$  is as follows for a mixture of oxygen atoms and molecules and  $\bar{\gamma}_s = 1.4$  (ref. 9):

$$\begin{aligned}
1.0039 &\leq A_1 \leq 1.0186 \\
0.9507 &\leq B_1 \leq 0.9507 \left( \sqrt{\frac{3}{4}} \frac{K_A}{m_A} + \sqrt{\frac{3}{2}} \frac{K_M}{m_M} \right) \bigg/ \left( \frac{K_A}{m_A} + \frac{K_M}{m_M} \right) \\
0.9056 &\leq C_1 \leq 0.9507
\end{aligned}$$

The minimum values for  $A_1$  and  $C_1$  occur at  $n_A = 0.5\rho/m_A$ , whereas the maximum value for  $B_1$  occurs at this value of  $n_A$ .

Expressions (59), (61), and (62) reduce to those obtained in reference 9<sup>10</sup> if one assumes the values for  $A_1$ ,  $B_1$ , and  $C_1$  to be unity and a noncatalytic surface boundary condition as given by equation (63). The concentration slip boundary condition provided in reference 9 is

$$C_A^s = C_{A,e}^w + \frac{2 - \gamma_A}{2\gamma_A} \sqrt{\frac{2\pi m_A}{kT_s}} \mathcal{D}_{AM}^s \left( \frac{\partial C_A}{\partial n^*} \right)_s \quad (64)$$

which is the same as equation (55b) obtained herein except for the additive term  $C_{A,e}^w$ .<sup>11</sup> It is obvious that the temperature slip boundary condition of equation (2.8c) obtained in reference 9 is

<sup>10</sup> See appendix C for the dimensional form of the slip boundary conditions given in reference 9.

<sup>11</sup> It appears that equation (2.8d) of reference 9 for the concentration slip has been formulated for the chemical equilibrium wall condition. Thus, when surface slip goes to zero, one obtains from equation (2.8d) the equilibrium value for the concentration, i.e.,  $C_A = C_{A,e}^w$ , which would be zero for the oxygen atoms for surface temperatures of 2000 K or less. For a highly cooled wall, the equilibrium catalytic wall condition can be approximated by a fully catalytic wall condition where the species concentrations are set equal to the cold gas equilibrium value.

valid, strictly speaking, for a noncatalytic surface only and is not consistent with the concentration slip boundary condition of equation (2.8d) (reproduced here as equation (64)) obtained for a finite catalytic wall. As a matter of fact, the velocity and temperature slip boundary conditions of reference 9 are similar to those of reference 10,<sup>12</sup> where these slip conditions are provided for a perfect gas (or single-species gas).

The inconsistencies in the boundary conditions used in references 11 and 12 are similar to those of reference 10, namely, the pressure and temperature slip values are in error by the ratio of dimensionless thermal conductivity to the viscosity  $K/\mu$ . References 11 and 12 also employ the single-species formulation for obtaining the velocity, temperature, and pressure slip values, and the concentration slip expression in these references is the one obtained for a binary mixture (ref. 9). The coefficients appearing in the slip equations of reference 12 may be obtained by multiplying  $a_1$ ,  $b_1$ , and  $c_1$  (coefficients of ref. 9) given here by  $16/5\pi$ . The factor  $16/5$  is sometimes replaced by  $\pi$ .

### Simplifications for Single-Species Gas

Equations (39) through (42) and equation (43b) may be simplified for a single-species gas to the expressions obtained in reference 6. For single species, these simplified equations may be written as (with  $\gamma_A = 0$  and  $M_{iy} = 0$  for a single-species gas).

Density slip:

$$\frac{\rho_s}{\rho_w} = \frac{\bar{m}\bar{n}^s}{\bar{m}\bar{n}^w} = \sqrt{\frac{T_w}{T_s}} \left[ 1 + \frac{5}{24} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right]^{-1} \quad (65)$$

Pressure slip:

$$\frac{p^s}{p^w} = \left\{ 1 - \left[ \frac{2 - \theta}{\theta} \frac{15}{16} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s + \frac{5}{12} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right] \right\}^{-1} \quad (66)$$

Velocity slip:

$$v_{0x}^s = \frac{2 - \theta}{\theta} \frac{5\pi}{16} \lambda_s \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right)_s + \frac{15}{32} \sqrt{\frac{\pi}{2}} \sqrt{RT_s} \left( \frac{\lambda}{T} \frac{\partial T}{\partial x} \right)_s \quad (67)$$

$$v_{0z}^s = \frac{2 - \theta}{\theta} \frac{5\pi}{16} \lambda_s \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right)_s + \frac{15}{32} \sqrt{\frac{\pi}{2}} \sqrt{RT_s} \left( \frac{\lambda}{T} \frac{\partial T}{\partial z} \right)_s \quad (68)$$

Temperature slip:<sup>13</sup>

$$\frac{T_s}{T_w} = \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \left[ -\frac{1}{2} + \frac{3}{4} \left( \frac{P_y}{p^s} + 1 \right) - \frac{75\pi}{128} \frac{2 - \theta}{\theta} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s \right]^{-1} \quad (69)$$

<sup>12</sup> There appears to be some error with the form of equations (2.7c) and (2.7d) given in reference 10 if one employs the definition from equation (2.4b) of the same reference of dimensionless heat-transfer rate  $q$  in these equations. (The Reynolds number parameter  $\epsilon^2$  is missing in eqs. (2.2b) and (2.4b) of the same reference for dimensionless shear stress and heat transfer, respectively. These have been corrected in ref. 9.) The resulting pressure and temperature slip expressions contain the dimensionless viscosity coefficient  $\mu$  rather than the dimensionless thermal conductivity  $K$ . References 11 and 12 contain same error. See equation (2.8c) of reference 9 for the "correct" form.

<sup>13</sup> Since the temperature slip expression contained in reference 6 is for a gas consisting of perfectly elastic spherical molecules, the gas does not possess any internal degree of freedom. Therefore, we have obtained the temperature slip equation from equation (43b).

where we have used the following relations between the coefficients of viscosity and thermal conductivity and the mean free path for perfectly elastic spherical molecules (ref. 13):

$$\mu = \frac{5}{16} \rho \lambda \sqrt{2\pi RT} \quad (70a)$$

$$K = \frac{15}{4} \frac{k}{\bar{m}} \mu \quad (70b)$$

The expression for  $\mu$  given earlier, following equation (25), for a single-species mixture is modified to

$$\mu = \frac{1}{2} \bar{n} k T b_0 \quad (70c)$$

Now, if an assumption is made that the slip values are *small*, equations for the density, pressure, and temperature slip are simplified to

Density slip:

$$\frac{\rho_s}{\rho_w} = \sqrt{\frac{T_w}{T_s}} \left[ 1 - \frac{5}{24} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right] \quad (71)$$

Pressure slip:

$$\frac{p^s}{p^w} = 1 + \frac{2 - \theta}{\theta} \frac{15}{16} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{12} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \quad (72)$$

Temperature slip:

$$\frac{T_s}{T_w} = -\frac{1}{4} \left( \frac{P_y}{p^s} + 1 \right) + \frac{3}{8} \left( \frac{P_y}{p^s} + 1 \right)^2 + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \frac{75\pi}{128} \frac{2 - \theta}{\theta} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s \quad (73a)$$

or

$$\frac{T_s}{T_w} = 1 + \frac{2 - \theta}{\theta} \frac{75\pi}{128} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{48} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{RT_s} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \quad (73b)$$

In obtaining equation (73b) from equation (73a), we have used  $P_y/p^s \approx 1$  in the second-order terms (i.e., 2d and 3d terms on right side of eq. (73a)). Equations (67), (68), (72), and (73b) are the slip equations given in references 6 and 13.

## No-Slip Boundary Condition for Species Concentration

### Multicomponent Mixture

The no-slip boundary condition for the species concentration without any assumptions may be obtained from equations (44) and (45). In the absence of slip, the thickness of the Knudsen layer shrinks to zero and the values at the top of the Knudsen layer become the wall values (see fig. 1):

$$n_i^w = \frac{\rho_w}{m_i} \left\{ 1 + \frac{1}{\bar{m}} \left[ \left( \frac{\partial C_i}{\partial y} \right)_w + \frac{1}{m_i} \left( \frac{\psi_i}{\mathcal{D}_{AM}} \right)_w \right] / \sum_{q=1}^{NS} \left( \frac{1}{m_q} \frac{\partial C_q}{\partial y} \right)_w \right\} \quad (74)$$

with

$$\psi_A^w = -\frac{2\gamma_A}{2 - \gamma_A} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^w}{2\bar{n}_w} \sqrt{\frac{2kT_w}{m_A}} \quad (A = \text{O}, \text{N}) \quad (75a)$$

$$\psi_M^w = -\psi_A^w \quad \left( \begin{array}{l} A = \text{O for } M = \text{O}_2 \\ A = \text{N for } M = \text{N}_2 \end{array} \right) \quad (75b)$$

$$\psi_i^w = 0 \quad (\text{For all other species}) \quad (75c)$$

where we have neglected the higher order shear (i.e.,  $P_y/p^w \approx 1$ ).

It is suggested here, again, that the concentration for the major species (for example, nitrogen) be obtained by requiring the sum of concentrations of all the species to equal unity.

For the recombining O and N atoms, equation (74) may further be simplified to

$$n_A^w = \frac{1}{k_{wA}} \left\{ \bar{n} \mathcal{D}_{AM} \left[ \frac{\partial C_A}{\partial y} + (1 - C_A) \sum_{q=1}^{\text{NS}} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right] \right\}_w \quad (76)$$

The recombination rate constant  $k_{wA}$  in equation (76) has been defined as (ref. 2)

$$k_{wA} = \frac{2\gamma_A}{2 - \gamma_A} \sqrt{\frac{kT_w}{2\pi m_A}} \quad (77)$$

without slip and higher order shear.

For a noncatalytic wall (with  $\gamma_A = 0$ ), equation (49) gives

$$\left( \frac{\partial C_i}{\partial y} \right)_w = 0 \quad (78)$$

for all the species of a multicomponent mixture.

### Binary Mixture

For a two-species mixture of atoms and molecules, equation (55b) gives

$$C_A^w = \frac{1}{k_{wA}} \left( \mathcal{D}_{AM} \frac{\partial C_A}{\partial y} \right)_w \quad (79)$$

for a surface with finite catalyticity and

$$\left( \frac{\partial C_A}{\partial y} \right)_w = 0 \quad (80)$$

for a noncatalytic surface. Equations (79) and (80) are used in reference 4.

Appendixes D and E give the slip and no-slip boundary conditions (presented in the text earlier), in the dimensionless form for the body-fitted and spherical polar coordinates, respectively, for a planar flow. The various integrals employed for evaluation of the net, incident, and specularly reflected fluxes defined by equations (5), (6), and (7), respectively, are given in appendix F.

## Discussion

The present analysis provides a consistent formulation for the slip equations for multicomponent and binary mixtures and single-species gas reacting catalytically on the surface. The differences between the slip expressions obtained by various researchers have been reconciled, and the implication of various assumptions (some of them inconsistent) contained in those expressions is discussed. The slip equations have also been obtained in body-fitted and spherical polar coordinates in a form which can readily be employed in the flow-field calculations.

Usually, the equation for pressure slip is not required as a boundary condition but is needed to obtain the surface pressure. The temperature slip equation given herein is for a constant surface temperature, which is provided as a boundary condition. For an adiabatic surface, however, the slip temperature  $T_s$  may be obtained by equating the wall heat-transfer rate to zero; that is

$$\dot{q}_w = \left( K \frac{\partial T}{\partial y} - \sum_{i=1}^{NS} J_i h_i + \mu v_{0x} \frac{\partial v_{0x}}{\partial y} \right)_s = 0$$

where the expression for mass flux  $J_i$  is provided in appendix B and the higher order terms have been dropped. The temperature slip equation is now required to obtain the wall temperature  $T_w$ .

An expression has also been obtained for the finite-rate species-concentration boundary condition for a multicomponent gas mixture without surface slip. This boundary condition in the literature (ref. 4) has generally been specified by assuming the dissociated air to be a binary mixture. However, the binary mixture formulation does not provide boundary conditions for the recombined molecules (on the surface) such as  $O_2$  and  $N_2$  in a multicomponent mixture; it gives boundary conditions only for the recombining atoms.

To assess the importance of various terms in the general boundary conditions suggested herein, a study is being undertaken in which the flow properties and boundary conditions would be varied systematically. The boundary equations form a simultaneous set, which is being coupled with a flow-field calculation procedure in the stagnation region. These equations would finally be coupled with the viscous shock-layer code developed by Moss (ref. 14) for the detailed flow-field calculations. The boundary equations obtained in the present work should provide a more realistic set of boundary conditions for a multicomponent mixture for low Reynolds number slip flows as well as no-slip flows.

## Concluding Remarks

The boundary slip expressions obtained in this paper are closed-form solutions of the mass, momentum, and energy flux equations by using the Chapman-Enskog velocity distribution function. This function represents a solution of the Boltzmann equation in the Navier-Stokes approximation. The analysis, obtained for nonequilibrium multicomponent airflow, includes the finite-rate surface catalytic recombination and changes in the internal energy during reflection from the surface. Expressions for the various slip quantities have been obtained in a form which can readily be employed in flow-field computations. A consistent set of equations is provided for multicomponent and binary mixtures and single-species gas. An expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture in the absence of slip.

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## Appendix A

### Constants Appearing in Distribution Function and Diffusion Velocity in Terms of Transport Properties

#### General Expressions for Sonine Expansion Coefficients

The Sonine expansion coefficients  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  appearing in the general velocity distribution function are found by a variational technique in which they are solutions to sets of simultaneous equations. References 2 and 7 provide the coefficients in terms of solutions to these sets of equations. These solutions are expressed in terms of the collision integrals  $\Omega_{ij}^{(s,\ell)}$ . Reference 7 also provides the transport properties in terms of the Sonine expansion coefficients. Thus, in place of evaluating these coefficients in terms of the collision integrals, they may be expressed in terms of the transport properties. The various relations are

(i) For  $a_{i0}$ ,

$$D_i^T(\xi) = \frac{n_i m_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0}(\xi) \quad (\text{A1})$$

(ii) For  $a_{i1}$ ,

$$K(\xi) = -\frac{5}{4} k \sum_{i=1}^{\text{NS}} n_i \sqrt{\frac{2kT}{m_i}} a_{i1}(\xi) \quad (\text{A2})$$

(iii) For  $b_{i0}$ ,

$$\mu(\xi) = \frac{1}{2} kT \sum_{i=1}^{\text{NS}} n_i b_{i0}(\xi) \quad (\text{A3})$$

(iv) For  $c_{i0}^{(j)}$ , in the distribution function used here, the Kernel  $C_i^{(j)} - C_i^{(k)}$  has associated Sonine polynomial coefficients  $c_{im}^{(j,k)}$ . Now  $C_i^{(i)} = 0$  (see ref. 7), then  $c_{i0}^{(j)} \equiv c_{i0}^{(j,i)}$  and

$$D_{ij}(\xi) = \frac{\rho n_i}{2\bar{n}m_j} \sqrt{\frac{2kT}{m_i}} c_{i0}^{(j)}(\xi) \quad (\text{A4})$$

where  $D_i^T(\xi)$ ,  $K(\xi)$ ,  $\mu(\xi)$ , and  $D_{ij}(\xi)$  are the multicomponent thermal diffusion coefficient, thermal conductivity, coefficient of viscosity, and the multicomponent diffusion coefficient, respectively. The argument  $\xi$  is the number of terms used in the Sonine expansion. Except for  $D_i^T$ , letting  $\xi = 1$  gives quite good results for  $K$ ,  $\mu$ , and  $D_{ij}$ . When  $\xi = 1$ , however, coefficients  $D_i^T$  vanish. Hence, in order to get the coefficient of thermal diffusion, it is necessary to take at least two terms in the Sonine expansion (i.e.,  $\xi = 2$ ). If the argument does not appear with a coefficient (except for  $a_{i0}$ ), it is considered to have one term in the Sonine expansion.

The diffusion velocity for  $i$ th species in terms of the transport coefficients is obtained as (see ref. 7)

$$\bar{V}_k^i = \frac{\bar{n}^2}{n_i \rho} \sum_{j=1}^{\text{NS}} m_j D_{ij} d_k^j - \frac{1}{n_i m_i} D_i^T \frac{\partial \ln T}{\partial x_k} \quad (\text{A5})$$

where the diffusion vector  $d_k^j$  for the  $j$ th species is defined after neglecting the external forces as (see eq. (16)):

$$d_k^j = \frac{\partial}{\partial x_k} \left( \frac{n_j}{\bar{n}} \right) + \left( \frac{n_j}{\bar{n}} - \frac{n_j m_j}{\rho} \right) \frac{\partial \ln p}{\partial x_k} \quad (\text{A6})$$

Equation (A6) may be simplified to obtain

$$d_k^j = \frac{\rho^2}{\bar{n}^2 m_j} \left( \frac{1}{\bar{m}} \frac{\partial C_j}{\partial x_k} - C_j \sum_{q=1}^{\text{NS}} \frac{1}{m_q} \frac{\partial C_q}{\partial x_k} \right) \quad (\text{A7})$$

### Simplified Expressions for Coefficients $a_{i1}$ and $b_{i0}$

Since  $a_{i1}$  and  $b_{i0}$  cannot be obtained directly from equations (A2) and (A3), we introduce the following assumptions for the mixture thermal conductivity and viscosity, respectively,

$$K \approx \sum_{i=1}^{\text{NS}} \frac{n_i}{\bar{n}} K_i \quad (\text{A8})$$

$$\mu \approx \sum_{i=1}^{\text{NS}} \frac{n_i}{\bar{n}} \mu_i \quad (\text{A9})$$

Equations (A8) and (A9) are approximate forms for the more exact formula of Wilke. (See ref. 15.) These equations imply that

$$\sum_{j=1}^{\text{NS}} \frac{n_j}{\bar{n}} \phi_{ij} \approx 1 \quad (\text{A10})$$

in Wilke's relation. This relation is approximately true for air.

Thus, with the help of equations (A2), (A3), (A8), and (A9), we may obtain the following approximate expressions for  $a_{i1}$  and  $b_{i0}$ , respectively,

$$n_i a_{i1} \approx -\frac{4}{5} \frac{n_i}{\bar{n}} \frac{K_i}{k} \sqrt{\frac{m_i}{2kT}} \quad (\text{A11})$$

$$n_i b_{i0} \approx \frac{2}{kT} \frac{n_i}{\bar{n}} \mu_i \quad (\text{A12})$$

For accurate evaluations of  $a_{i1}$  and  $b_{i0}$ , cumbersome expressions of the type of equation (7.4-49) of reference 7 are required to be solved.

## Appendix B

### Evaluated Expressions for Fluxes of Mass, Momentum, and Energy From Integrals Over Velocity Distribution Function

The fluxes of mass, momentum, and energy (i.e., of a property  $\phi^i(\mathbf{V})$ ) are given in terms of integrals over the velocity distribution function  $f^i(\mathbf{V})$  in the section "Analysis" of the main text. Here we give evaluated forms for these fluxes obtained from integration over the distribution functions. The various integrals needed in these evaluations are provided in appendix F.

(i) Expressions for mass flux of species:

Net

$$M_{ik} = \frac{m_i n_i^s}{2} \left( \frac{2kT_s}{m_i} \right)^{1/2} \left( -\frac{\partial \ln T}{\partial x_k} a_{i0} + n \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_k^j \right)_s \quad (k = x, y, z) \quad (\text{B1})$$

Incident

$$M_i^\downarrow = -\frac{m_i n_i^s}{2\sqrt{\pi}} \left( \frac{2kT_s}{m_i} \right)^{1/2} \left[ 1 + \frac{b_{i0}}{6} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{1}{2} M_{iy} \quad (\text{B2})$$

Specularly reflected

$$M_i^\uparrow = -M_i^\downarrow \quad (\text{B3})$$

Diffusely reflected

$$M_i^w = \frac{m_i n_i^w}{2\sqrt{\pi}} \left( \frac{2kT_w}{m_i} \right)^{1/2} \quad (\text{B4})$$

It may be mentioned that  $M_{iy}$  as obtained here is similar to the mass flux  $J_i$  expression of reference 16.

(ii) Correlation with Blottner's expression (ref. 16) for mass flux:

If the thermal diffusion term is neglected in equation (B1) and substitutions are made for  $c_{i0}^{(j)}$  and  $d_k^j$  from equations (A4) and (A7), equation (B1) may be simplified to obtain<sup>14</sup>

$$J_i \equiv M_{iy} = \frac{\rho W_i}{\bar{W}} \sum_{j \neq i}^{\text{NS}} D_{ij} \left( \frac{\partial C_j}{\partial y} - C_j \bar{W} \sum_{q=1}^{\text{NS}} \frac{1}{W_q} \frac{\partial C_q}{\partial y} \right) \quad (\text{B5})$$

where  $W_i$  is the molecular (or atomic) weight of the  $i$ th species and is related to the mass of the  $i$ th species  $m_i$  through the relation

$$\frac{m_i}{W_i} = \frac{k}{\mathcal{R}} \quad (\text{B6})$$

Here  $k$  is the Boltzmann constant and  $\mathcal{R}$  is the universal gas constant. Equation (B5) may also be written as

$$J_i = \rho \frac{W_i}{\bar{W}} \sum_{j=1}^{\text{NS}} \left( D_{ij} - \frac{\bar{W}}{W_j} \sum_{q \neq i}^{\text{NS}} D_{iq} C_q \right) \frac{\partial C_j}{\partial y} \quad (\text{B7a})$$

<sup>14</sup> It may be noted here that  $D_{ii} = 0$ . See reference 7 for details.

or, with the introduction of the multicomponent Lewis number  $N_{Le,ij}$  defined as

$$N_{Le,ij} = \frac{\rho c_p D_{ij}}{K} = \frac{\rho N_{Pr} D_{ij}}{\mu}$$

Equation (B7a) may be rewritten as

$$J_i = \frac{\mu}{N_{Pr}} \sum_{j=1}^{NS} \left( \frac{W_i}{\bar{W}} N_{Le,ij} - \frac{W_i}{W_j} \sum_{q \neq i}^{NS} N_{Le,iq} C_q \right) \frac{\partial C_j}{\partial y} \quad (\text{B7b})$$

$$J_i = \frac{\mu}{N_{Pr}} \sum_{j \neq i}^{NS} \left[ \frac{W_i}{\bar{W}} N_{Le,ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} N_{Le,iq} C_q \right] \frac{\partial C_j}{\partial y} \quad (\text{B7c})$$

$$J_i = -\frac{\mu}{N_{Pr}} \left( N_{Le,i} \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \left\{ N_{Le,i} - \left[ \frac{W_i}{\bar{W}} N_{Le,ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} N_{Le,iq} C_q \right] \right\} \frac{\partial C_j}{\partial y} \right) \quad (\text{B7d})$$

or

$$J_i = -\frac{\mu}{N_{Pr}} \left( N_{Le,i} \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \bar{\Delta} b_{ij} \frac{\partial C_j}{\partial y} \right) \quad (\text{B7e})$$

where

$$\bar{\Delta} b_{ij} = N_{Le,i} - \left[ \frac{W_i}{\bar{W}} N_{Le,ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} N_{Le,iq} C_q \right] \quad (\text{B8})$$

In general,<sup>15</sup>

$$N_{Le,ij} = N_{Le,ij}(C_i, M_i, M_j, \mathcal{N}_{Le,ij})$$

If the binary Lewis numbers  $\mathcal{N}_{Le,ij}$  are assumed to be the same for all the species, then

$$N_{Le,ij} = N_{Le,ij}^* = N_{Le,ij}^*(C_i, M_i, M_j)$$

and equation (B8) for  $\bar{\Delta} b_{ij}$  becomes

$$\bar{\Delta} b_{ij}^* = N_{Le,i} - \left[ \frac{W_i}{\bar{W}} N_{Le,ij}^* + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} N_{Le,iq}^* C_q \right] \quad (\text{B9})$$

and the mass flux (eq. (B7e)) now becomes

$$J_i = -\frac{\mu}{N_{Pr}} \left( N_{Le,i} \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \bar{\Delta} b_{ij}^* \frac{\partial C_j}{\partial y} \right) \quad (\text{B10})$$

<sup>15</sup> See equations (7) and (8) of reference 16.

Further, if the binary Lewis numbers  $\mathcal{N}_{Le,ij}$  are constant for all the species, the term

$$\sum_{j \neq i}^{\text{NS}} \bar{\Delta} b_{ij}^* \frac{\partial C_j}{\partial y}$$

is zero in equation (B10). Therefore,

$$\sum_{j \neq i}^{\text{NS}} N_{Le,i} \frac{\partial C_j}{\partial y} = \sum_{j \neq i}^{\text{NS}} \left[ \frac{W_i}{\bar{W}} N_{Le,ij}^* + \left(1 - \frac{W_i}{W_j}\right) \sum_{q \neq i}^{\text{NS}} N_{Le,iq}^* C_q \right] \frac{\partial C_j}{\partial y} \quad (\text{B11a})$$

or

$$N_{Le,i} = - \left\{ \sum_{j \neq i}^{\text{NS}} \left[ \frac{W_i}{\bar{W}} N_{Le,ij}^* + \left(1 - \frac{W_i}{W_j}\right) \sum_{q \neq i}^{\text{NS}} N_{Le,iq}^* C_q \right] \frac{\partial C_j}{\partial y} \right\} \left( \frac{\partial C_i}{\partial y} \right)^{-1} \quad (\text{B11b})$$

Thus, equation (B10) gives the mass flux due to concentration gradients only with  $\Delta b_{ij}^*$  and  $N_{Le,i}$  defined by equations (B9) and (B11b), respectively.

To utilize equations (B9) and (B11b),  $N_{Le,ij}^*$  is still to be evaluated through complex matrix inversions (ref. 16). If we now make a little stronger assumption such that  $N_{Le,ij}^* = N_{Le,AM} = N_{Le}$  (same for all the species), we obtain a much simpler expression for  $\Delta b_{ij}^*$ , and equation (B11b) becomes

$$N_{Le,i} = N_{Le} \left[ \frac{W_i}{\bar{W}} - (1 - C_i) \left( \frac{\partial C_i}{\partial y} \right)^{-1} \sum_{j \neq i}^{\text{NS}} \left(1 - \frac{W_i}{W_j}\right) \frac{\partial C_j}{\partial y} \right] \quad (\text{B12a})$$

or

$$N_{Le,i} = N_{Le} \left[ \frac{W_i}{\bar{W}} + (1 - C_i) \left( \frac{\partial C_i}{\partial y} \right)^{-1} \sum_{j=1}^{\text{NS}} \frac{W_i}{W_j} \frac{\partial C_j}{\partial y} \right] \quad (\text{B12b})$$

Similarly the expression for  $\bar{\Delta} b_{ij}^*$  may be obtained from equation (B9) as

$$\bar{\Delta} b_{ij}^* = N_{Le,i} - N_{Le} \left[ \frac{W_i}{\bar{W}} + \left(1 - \frac{W_i}{W_j}\right) (1 - C_i) \right] \quad (\text{B13})$$

It may be noted that for  $\frac{\partial C_i}{\partial y} = 0$ , the term  $N_{Le,i} \frac{\partial C_i}{\partial y}$  in equation (B10) vanishes and equation (B11b) or (B12b) is not required. Further, employing a constant value for the Lewis number  $N_{Le}$  ( $= \frac{\rho N_{Pr} D_{AM}}{\mu}$ ), does not imply that  $N_{Le,i}$  has a constant value.

It should be pointed out here that for the case when  $\mathcal{N}_{Le,ij}$  is the same for all the species, we have used the condition

$$\sum_{j \neq i}^{\text{NS}} \bar{\Delta} b_{ik}^* \frac{\partial C_j}{\partial y} = 0$$

(and not just  $\bar{\Delta} b_{ik}^* = 0$  as employed in ref. 16) to obtain equation (B11b) for  $N_{Le,i}$ . The present formulation appears to provide a more consistent expression for  $N_{Le,i}$ .

Finally, equations (B10), (B12b), and (B13) for a binary (two-species) mixture give

$$J_i = -\frac{\mu}{NPr} NLe \frac{\partial C_i}{\partial y} \quad (\text{B14})$$

which is Fick's law for mass flux

$$N_{Le,i} = NLe \quad (\text{B15})$$

$$\overline{\Delta b_{ij}^*} = 0 \quad (\text{B16})$$

(iii) Expressions for normal momentum flux:

Net

$$P_{iy} = p_i^s \left[ 1 + \frac{b_{i0}}{3} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \quad (\text{B17a})$$

$$P_{iy} = p_i^s \left[ 1 + \tau_{yy}^i \right]_s \quad (\text{B17b})$$

where  $\tau_{k\ell}^i$  represents terms in the stress tensor for the  $i$ th species.

Incident and specularly reflected

$$\begin{aligned} P_{iy}^\downarrow = P_{iy}^\uparrow = p_i^s & \left[ \frac{1}{2} + \frac{b_{i0}}{6} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right. \\ & \left. + \frac{1}{\sqrt{\pi}} \frac{\partial \ln T}{\partial y} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \frac{\bar{n}}{\sqrt{\pi}} \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_y^j \right]_s \end{aligned} \quad (\text{B18})$$

Diffusely reflected

$$P_{iy}^w = \frac{1}{2} p_i^w \quad (\text{B19})$$

(iv) Expressions for tangential momentum flux:

Net

$$P_{ix} = -p_i^s \left[ \frac{b_{i0}}{2} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s \quad (\text{B20})$$

$$P_{iz} = -p_i^s \left[ \frac{b_{i0}}{2} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s \quad (\text{B21})$$

Incident and specularly reflected

$$\begin{aligned} P_{ix}^\downarrow = -P_{ix}^\uparrow = \frac{1}{\sqrt{\pi}} p_i^s & \left[ -w_{0x} - \sqrt{\pi} \frac{b_{i0}}{4} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right. \\ & \left. + \frac{1}{2} \frac{\partial \ln T}{\partial x} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \frac{\bar{n}}{2} \sum_{j=1}^{\text{NS}} c_{i0}^{(j)} d_x^j \right]_s \end{aligned} \quad (\text{B22})$$

$$\begin{aligned}
P_{iz}^\downarrow = -P_{iz}^\uparrow = \frac{1}{\sqrt{\pi}} p_i^s & \left[ -w_{0z} - \sqrt{\pi} \frac{b_{i0}}{4} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right. \\
& \left. + \frac{1}{2} \frac{\partial \ln T}{\partial z} \left( a_{i0} - \frac{1}{2} a_{i0} \right) - \frac{\bar{n}}{2} \sum_{j=1}^{NS} c_{i0}^{(j)} d_z^j \right]_s
\end{aligned} \tag{B23}$$

Diffusely reflected

$$P_{ix}^w = P_{iz}^w = 0 \tag{B24}$$

(v) Expressions for energy flux:

Net

$$E_{ik} = \frac{5}{4} \frac{2kT_s}{m_i} \left[ \frac{m_i n_i}{2} \left( \frac{2kT}{m_i} \right)^{1/2} \frac{\partial \ln T}{\partial x_k} a_{i1} + M_{ik} \right]_s \quad (k = x, y, z) \tag{B25a}$$

$$E_{ik} = \dot{q}_{ik} + \frac{5}{2} \left( \frac{kT_s}{m_i} \right) M_{ik} \tag{B25b}$$

where

$$\dot{q}_{ik} = - \left( \frac{n_i K_i}{\bar{n}} \frac{\partial T}{\partial x_k} \right)_s$$

Incident and specularly reflected

$$E_i^\downarrow = -E_i^\uparrow = -\frac{m_i n_i^s}{2\sqrt{\pi}} \left( \frac{2kT_s}{m_i} \right)^{3/2} \left[ 1 + \frac{b_{i0}}{4} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{1}{2} E_{iy} \tag{B26}$$

Diffusely reflected

$$E_i^w = \frac{m_i n_i^w}{2\sqrt{\pi}} \left( \frac{2kT_w}{m_i} \right)^{3/2} \tag{B27}$$

## Appendix C

### Slip Boundary Conditions Given by Davis for Binary Mixture

In this appendix, the dimensional form of the slip boundary conditions obtained by Davis (refs. 9 and 10) is provided for the purpose of comparison with the slip expressions obtained in the main text for a binary mixture.

The dimensionless form of the surface slip conditions provided in references 9 and 10 are

Concentration slip (ref. 9):<sup>16</sup>

$$C_A^s = C_{A,e}^w + \varepsilon^2 \sqrt{\frac{\pi W_A}{2\bar{W}}} \frac{2 - \gamma_A}{\gamma_A} \frac{(\bar{F}_D)_s}{\bar{p}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial C_A}{\partial \bar{n}} \right)_s \quad (C1)$$

Velocity slip (ref. 9):

$$\bar{u}_s = \varepsilon^2 a_1 \frac{\bar{\mu}_s}{\bar{p}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} \right)_s \quad (C2)$$

Pressure slip (ref. 10):<sup>17</sup>

$$\bar{p}_s = \bar{p}_w + \varepsilon^2 b_1 \frac{\bar{K}_s}{\bar{T}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (C3)$$

Temperature slip (ref. 9):

$$\bar{T}_s = \bar{T}_w + \varepsilon^2 c_1 \frac{\bar{K}_s}{\bar{p}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (C4)$$

With the help of the nondimensionalizing quantities given in references 9 and 10, the following dimensional forms of equations (C1) through (C4) are obtained:

Concentration slip:

$$C_A^s = C_{A,e}^w + \frac{2 - \gamma_A}{2\gamma_A} \sqrt{\frac{2\pi m_A}{kT_s}} \left( \mathcal{D}_{AM} \frac{\partial C_A}{\partial n^*} \right)_s \quad (C5)$$

Velocity slip:

$$u_s = a_1 \frac{\mu_s}{\sqrt{kT_s}} \left( \frac{1}{\bar{n}\sqrt{\bar{m}}} \frac{\partial u}{\partial n^*} \right)_s \quad (C6)$$

Pressure slip:

$$p_s = p_w + b_1 \left( \frac{\bar{\gamma} - 1}{\bar{\gamma}} \right)_s \sqrt{\frac{\bar{m}}{kT_s}} \left( K \frac{\partial T}{\partial n^*} \right)_s \quad (C7)$$

Temperature slip:

$$T_s = T_w + c_1 \left( \frac{\bar{\gamma} - 1}{\bar{\gamma}} \right)_s \left( \frac{K}{k} \frac{1}{\sqrt{kT}} \frac{\partial T}{\partial n^*} \right) / \left( \frac{\bar{n}}{\sqrt{\bar{m}}} \right)_s \quad (C8)$$

<sup>16</sup> Here the dimensionless quantities are denoted with a bar over the symbol. See appendix D for details of nondimensionalization and the coordinate system.

<sup>17</sup> For the reasons explained in the main text, we have employed  $\bar{K}$  in place of  $\bar{\mu}$  in this expression.

where  $n^*$  is the coordinate normal to the surface (see fig. D1), and  $\bar{n}$  and  $\bar{m}$  are the number density and mass of a mixture molecule, respectively. The constants  $a_1$ ,  $b_1$ , and  $c_1$  are defined as

$$a_1 = \frac{5\pi}{16} \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} = 1.2304 \frac{2-\theta}{\theta}$$
$$b_1 = \frac{15}{16} \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} = 1.1750 \frac{2-\theta}{\theta}$$
$$c_1 = \frac{75\pi}{128} \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} = 2.3071 \frac{2-\theta}{\theta}$$

## Appendix D

### Slip Conditions in Body-Oriented Coordinate System

In this appendix, we obtain the slip conditions for an axisymmetric body in the body-oriented coordinate  $(s^*, n^*)$  system. The coordinate configuration for such a system is given in figure D1. The equations of this appendix contain simplifications similar to those given in the section "Simplifications for Multicomponent Mixture" in the main text. By employing the metric coefficients (ref. 17) of  $h_1 = 1 + n^* \kappa$  and  $h_2 = 1$ , equations (39) through (45) give the following slip equations in the body-oriented coordinate system.

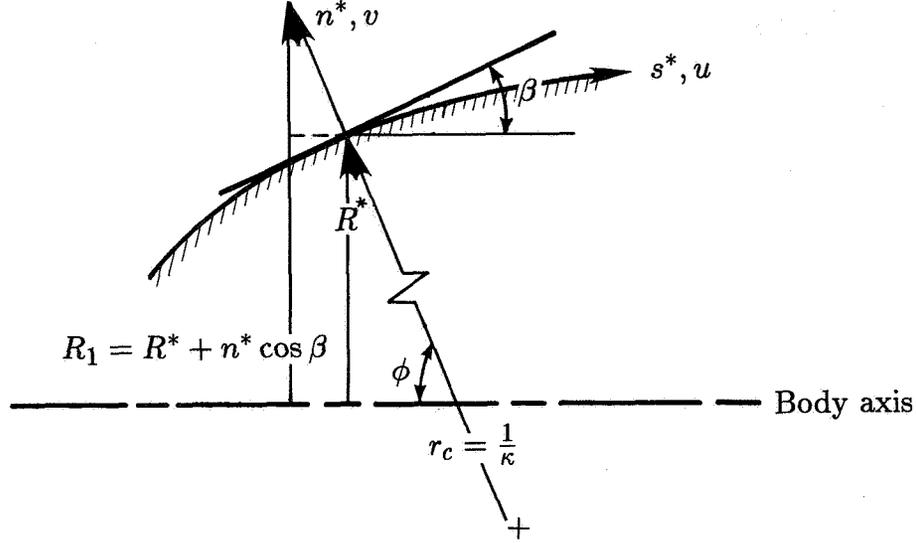


Figure D1. Coordinate configuration for body that is symmetric about its axis.

Concentration slip:

$$\frac{n_i^s}{n_i^w} = 2 \left( 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right) \sqrt{\frac{T_w}{T_s}} / \left( \frac{P_y}{p_s} + 1 \right) \quad (\text{D1})$$

where (from eqs. (35)) we define  $M_{iy}$  as

$$M_{Ay} = -k_{wA} n_A^w m_A \quad (A = O, N) \quad (\text{D2a})$$

$$M_{My} = k_{wA} n_A^w m_A \quad \begin{matrix} (A = O \text{ for } M = O_2) \\ (A = N \text{ for } M = N_2) \end{matrix} \quad (\text{D2b})$$

$$M_{iy} = 0 \quad (\text{For all other atoms and molecules}) \quad (\text{D2c})$$

Pressure slip:

$$p_s = \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{1}{1 + n^* \kappa} \frac{\partial u}{\partial s^*} - 2 \frac{\partial v}{\partial n^*} \right) \right]_s + \frac{2}{5} \frac{(2 - \theta)}{\sqrt{\pi}} \left( \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial n^*} \right. \right. \\ \times \left. \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right)_s + \frac{\theta}{2} p^w \left. \right\} / \left\{ \frac{\theta}{2} - \frac{2(2 - \theta)}{\sqrt{\pi}} \frac{D_{AM}}{\sqrt{2kT_s}} \right. \\ \times \left. \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial n^*} + (1 - C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial n^*} \right]_s \right\} \quad (\text{D3})$$

Velocity slip:

$$\begin{aligned}
u_s = & \left\{ \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial u}{\partial n^*} - \frac{\kappa u}{1+n^*\kappa} + \frac{1}{1+n^*\kappa} \frac{\partial v}{\partial s^*} \right) \right]_s \right. \\
& + \frac{1}{5} \left( \frac{1}{kT} \frac{1}{1+n^*\kappa} \frac{\partial T}{\partial s^*} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right)_s + n_s \mathcal{D}_{AM}^s \sum_{i=1}^{NS} \sqrt{m_i} \\
& \left. \times \left[ \frac{1}{1+n^*\kappa} \frac{\partial C_i}{\partial s^*} + (1-C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{1}{1+n^*\kappa} \frac{\partial C_q}{\partial s^*} \right]_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (D4)
\end{aligned}$$

Temperature slip:

$$\begin{aligned}
\frac{T_s}{T_w} = & \left[ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{\bar{n}_s} \times \sum_i \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \right. \\
& \left. \times \sum_i \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s \right] / \left[ -\sqrt{\pi} \frac{2-\theta}{\theta} \right. \\
& \left. \times \left( \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial n^*} - \frac{5}{4} \sum_{i=1}^{NS} \frac{M_{iy}}{\bar{n} m_i} - \frac{1}{\bar{n}} \times \sum_i \frac{M_{iy}}{m_i} \right)_s \right. \\
& \left. + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \times \sum_i \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s \right] \quad (D5)
\end{aligned}$$

If the internal energy (comprising rotational and vibrational energies in this case) is considered frozen during reflection from the surface, the following form of the temperature slip equation is obtained (see eq. (28) of ref. 5):

$$\begin{aligned}
\frac{T_s}{T_w} = & \left[ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s \right] / \left\{ -\sqrt{\pi} \frac{2-\theta}{\theta} \right. \\
& \left. \times \left[ \frac{1}{2} \left( \frac{K}{p} \frac{\partial T}{\partial n^*} \right)_s - \frac{5}{4} \sum_{i=1}^{NS} \left( \frac{M_{iy}}{\bar{n} m_i} \right)_s \right] + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \frac{\bar{m}_s}{m_i} C_i^s \right\} \quad (D6)
\end{aligned}$$

Equation for  $n_i^s$ :

$$n_i^s = \frac{\rho_s}{m_i} \left\{ 1 + \frac{1}{\bar{m}_s} \left[ \left( \frac{\partial C_i}{\partial n^*} \right)_s + \frac{1}{m_i} \left( \frac{\psi_i}{\mathcal{D}_{AM}} \right)_s \right] / \sum_{q=1}^{NS} \left( \frac{1}{m_q} \frac{\partial C_q}{\partial n^*} \right)_s \right\} \quad (D7)$$

where

$$\psi_A^s = -\frac{\gamma_A}{2-\gamma_A} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^s}{2\bar{n}_s} \sqrt{\frac{2kT_s}{m_A}} \left( \frac{P_{Ay}}{p^s} + 1 \right) \quad (A = \text{O, N}) \quad (\text{D8a})$$

$$\psi_M^s = -\psi_A^s \quad \left( \begin{array}{l} A = \text{O for } M = \text{O}_2 \\ A = \text{N for } M = \text{N}_2 \end{array} \right) \quad (\text{D8b})$$

$$\psi_i^s = 0 \quad (\text{For all other species}) \quad (\text{D8c})$$

In equations (D1), (D5), (D6), and (D8a), the ratio  $\frac{P_y}{p^s}$  is defined as

$$\frac{P_y}{p^s} = \left[ 1 + \frac{b_0}{3} \left( \frac{1}{1+n^*\kappa} \frac{\partial u}{\partial s^*} - 2 \frac{\partial v}{\partial n^*} \right) \right]_s \quad (\text{D9})$$

and  $b_0$  is related to viscosity  $\mu$  through the relation

$$\mu = \frac{1}{2} \bar{n} k T b_0 \quad (\text{D10})$$

which has been obtained from equation (A3) by assuming  $b_{i0}$  to be the same ( $b_0$ ) for all the species.

Equations (D1) through (D8) may now be nondimensionalized by using the following relations (refs. 9 and 14):

$$\begin{aligned} \bar{u} &= \frac{u}{U_\infty} & \bar{v} &= \frac{v}{U_\infty} & \bar{T} &= \frac{T}{U_\infty^2/c_{p,\infty}} = \frac{T}{T_{\text{ref}}} \\ \bar{p} &= \frac{p}{\rho_\infty U_\infty^2} & \bar{\rho} &= \frac{\rho}{\rho_\infty} & \bar{\mu} &= \frac{\mu}{\mu(T_{\text{ref}})} = \frac{\mu}{\mu_{\text{ref}}} \\ \bar{c}_p &= \frac{c_p}{c_{p,\infty}} & \bar{h} &= \frac{h}{U_\infty^2} & \bar{k}_{wi} &= \frac{k_{wi}}{U_\infty} \\ \bar{K} &= \frac{K}{c_{p,\infty} \mu_{\text{ref}}} & \bar{s} &= \frac{s^*}{r_N} & \bar{n} &= \frac{n^*}{r_N} \\ \bar{\kappa} &= \kappa r_N & \bar{R} &= \frac{R^*}{r_N} & \bar{M}_{iy} &= \frac{M_{iy}}{n_i^w m_i U_\infty} \\ \bar{\psi}_i &= \frac{\psi_i}{m_A \mathcal{D}_{AM}/r_N} & \bar{k}_{wA} &= \frac{k_{wA}}{U_\infty} \end{aligned}$$

where  $r_N$  is the body nose radius of curvature,  $T_{\text{ref}} = U_\infty^2/c_{p,\infty}$ , and  $\mu_{\text{ref}} = \mu(U_\infty^2/c_{p,\infty})$ . If the nondimensional quantities as defined here are used, the following equations are obtained from equations (D1) through (D8):

Concentration slip:

$$\frac{C_i^s}{C_i^w} = 2 \frac{\bar{\rho}_w}{\bar{\rho}_s} \left( 1 + \frac{1}{2} M_\infty \bar{M}_{iy} \sqrt{2\pi\bar{\gamma}_\infty \frac{W_i}{\bar{W}_\infty} \frac{T_\infty}{T_w}} \right) \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} / \left( \frac{P_y}{p^s} + 1 \right) \quad (\text{D11})$$

where

$$\bar{M}_{Ay} = -\bar{k}_w A \quad (A = O, N) \quad (D12a)$$

$$\bar{M}_{My} = \bar{k}_w A \frac{C^w_A}{C^w_M} \quad \begin{cases} (A = O \text{ for } M = O_2) \\ (A = N \text{ for } M = N_2) \end{cases} \quad (D12b)$$

$$\bar{M}_{iy} = 0 \quad (\text{For all other atoms and molecules}) \quad (D12c)$$

Pressure slip:

$$\begin{aligned} \bar{p}_s = & \left\{ \bar{p}_w - \varepsilon^2 \left[ \frac{2}{3} \bar{\mu} \left( \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right) \right]_s \right. \\ & + \varepsilon^2 \left[ \frac{2}{5\sqrt{\pi}} \frac{2-\theta}{\theta} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{1}{M_\infty (N_{Pr})_s} \sqrt{\frac{2T_{\text{ref}} \bar{T}_s \bar{W}_\infty}{\bar{\gamma}_\infty T_\infty \bar{W}_s}} \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \right. \\ & \times \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{\bar{W}_i} \right)^{3/2} \left. \left. C_i^s \bar{\mu}_i^s \right] \right\} / \left\{ 1 - \frac{4}{\sqrt{\pi}} \frac{2-\theta}{\theta} \varepsilon^2 \frac{(N_{Le})_s M_\infty}{(N_{Pr})_s} \right. \\ & \left. \times \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2T_{\text{ref}} \bar{T}_s}} \frac{\bar{\mu}_s}{\bar{\rho}_s} \sum_{i=1}^{\text{NS}} \sqrt{\frac{\bar{W}_i}{\bar{W}_\infty}} \left[ \frac{\partial C_i}{\partial \bar{n}} + (1 - C_i) \sum_{q=1}^{\text{NS}} \frac{\bar{W}}{\bar{W}_q} \frac{\partial C_q}{\partial \bar{n}} \right]_s \right\} \quad (D13) \end{aligned}$$

where we have assumed that  $N_{Pr} \approx N_{Pr,i}$  and

$$\frac{c_{p,i}}{R_i} = \frac{\bar{\gamma} - 1}{\bar{\gamma}}$$

Velocity slip:

$$\begin{aligned} \bar{u}_s = & \varepsilon^2 \frac{M_\infty \bar{\mu}_s}{\bar{\rho}_s} \left( \frac{1}{\sum_{i=1}^{\text{NS}} \sqrt{\frac{\bar{W}}{\bar{W}_i}} C_i} \right)_s \left\{ \sqrt{\pi} \frac{2-\theta}{\theta} \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2T_{\text{ref}} \bar{T}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1 + \bar{n}\bar{\kappa}} + \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial \bar{v}}{\partial \bar{s}} \right)_s \right. \\ & + \frac{1}{5} \frac{1}{M_\infty (N_{Pr})_s} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{\bar{T}} \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial T}{\partial \bar{s}} \right)_s \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{\bar{W}_i} \right)^{3/2} C_i^s \frac{\bar{\mu}_i^s}{\bar{\mu}_s} + \frac{(N_{Le})_s}{M_\infty (N_{Pr})_s} \\ & \left. \times \sum_{i=1}^{\text{NS}} \sqrt{\frac{\bar{W}_i}{\bar{W}_s}} \left[ \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial C_i}{\partial \bar{s}} + (1 - C_i) \sum_{q=1}^{\text{NS}} \frac{\bar{W}}{\bar{W}_q} \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial C_q}{\partial \bar{s}} \right]_s \right\} \quad (D14) \end{aligned}$$

Temperature slip:

$$\begin{aligned}
\frac{\bar{T}_s}{\bar{T}_w} = & \left\{ -\sqrt{\frac{\pi}{2}} \frac{\bar{\rho}_w}{\bar{p}_s \bar{\rho}_s} \left( \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} + \sum_i^{\text{Diatomic molecules}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right) + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \right. \\
& \times \left[ \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s + \sum_i^{\text{Diatomic molecules}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] \left. / \left\{ -\sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \right. \right. \\
& \times \left[ \frac{\varepsilon^2}{2\bar{\gamma}_\infty} \frac{1}{M_\infty^2 (N_{Pr})_s} \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{T_{\text{ref}}}{T_\infty} \sqrt{\frac{\bar{\rho}_s \bar{W}_\infty}{\bar{p}_s \bar{W}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s - \frac{5}{4} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right. \\
& \times \left. \left. \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} - \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_i^{\text{Diatomic molecules}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right] + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \right. \\
& \times \left. \left. \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_i^{\text{Diatomic molecules}} \left( \frac{W_s}{W_i} \right)^{3/2} C_i^s \right\} \quad (\text{D15})
\end{aligned}$$

or, with frozen internal energy during reflection from surface,

$$\begin{aligned}
\frac{\bar{T}_s}{\bar{T}_w} = & \left[ -\sqrt{\frac{\pi}{2}} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \right. \\
& \times \left. \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] / \left\{ -\sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\varepsilon^2}{2\bar{\gamma}_\infty} \frac{1}{M_\infty^2 (N_{Pr})_s} \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{T_{\text{ref}}}{T_\infty} \sqrt{\frac{\bar{\rho}_s}{\bar{p}_s}} \right. \right. \\
& \times \left. \left. \frac{\bar{W}_\infty}{\bar{W}_s} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s - \frac{5}{4} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right] \right. \\
& \left. + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right\} \quad (\text{D16})
\end{aligned}$$

Equation for  $n_i^s$ :

$$C_i^s = \frac{n_i^s m_i}{\rho_s} = 1 + \left( \frac{\partial C_i}{\partial \bar{n}} + \frac{W_A \bar{\psi}_i}{W_i} \right)_s / \sum_{q=1}^{\text{NS}} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_s \quad \begin{cases} (A = \text{O for } i = \text{O}_2) \\ (A = \text{N for } i = \text{N}_2) \end{cases} \quad (\text{D17})$$

where

$$\bar{\psi}_A^s = \frac{r_N \psi_A^s}{m_A \mathcal{D}_{AM}^s} = -\frac{\gamma_A}{2 - \gamma_A} \frac{1}{\varepsilon^2 M_\infty} \sqrt{\frac{\bar{W}_\infty T_s}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \times \frac{\bar{W}_s}{W_A} \left( \frac{N_{Pr}}{N_{Le}} \right)_s \left( \frac{\bar{p}}{\bar{\mu}} \right)_s \left( \frac{P_y}{p^s} + 1 \right) C_A^s \quad (A = O, N) \quad (D18a)$$

$$\bar{\psi}_M^s = -\bar{\psi}_A^s \quad \left( \begin{array}{l} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{array} \right) \quad (D18b)$$

$$\bar{\psi}_i^s = 0 \quad (\text{For all other species}) \quad (D18c)$$

$$\frac{P_y}{p^s} = \frac{\bar{P}_y}{\bar{p}^s} = 1 + \frac{2}{3} \frac{\bar{\gamma}_\infty T_\infty}{T_{\text{ref}}} \left( \frac{\bar{\mu}}{\bar{\rho} \bar{T}} \right)_s \varepsilon^2 M_\infty^2 \frac{\bar{W}_s}{\bar{W}_\infty} \left( \frac{1}{1 + \bar{n} \bar{\kappa}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right)_s \quad (D19a)$$

$$\frac{P_y}{p^s} = 1 + \frac{2}{3} \frac{\bar{\mu}_s}{\bar{p}_s} \varepsilon^2 \left( \frac{1}{1 + \bar{n} \bar{\kappa}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right)_s \quad (D19b)$$

and

$$W_i = \frac{m_i \mathcal{R}}{k}$$

Reynolds number parameter:

$$\varepsilon^2 = \frac{\mu_{\text{ref}}}{\rho_\infty U_\infty r N}$$

Prandtl number:

$$N_{Pr} = \frac{c_p \mu}{K}$$

Lewis number:

$$N_{Le} = \frac{\rho c_p \mathcal{D}_{AM}}{K}$$

Mach number:

$$M_\infty = \frac{U_\infty}{a_\infty}$$

Recombination rate constant:

$$\bar{k}_{wA} = \frac{\gamma_A}{M_\infty} \sqrt{\frac{\bar{W}_\infty T_s T_{\text{ref}}}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \sqrt{\frac{T_w}{\bar{T}_s T_{\text{ref}}}}$$

For a noncatalytic surface ( $\gamma_A = \bar{k}_{wA} = 0$ ), equations (D18) give  $\bar{\psi}_i^s = 0$  for all species. For this case, equation (D17) becomes

$$\left( \frac{\partial C_i}{\partial \bar{n}} \right)_s = -(1 - C_i^s) \sum_{q=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_s \quad (D20)$$

Equation (D20), similar to equation (47b), gives

$$\left( \frac{\partial C_i}{\partial \bar{n}} \right)_s = 0 \quad (D21)$$

which may be employed as the boundary condition for a noncatalytic surface with a multicomponent gas mixture (with the binary assumption for diffusion coefficients). For a fully catalytic surface, employing  $\gamma_A = 1$  and using equations (D18) in equation (D17) would yield the appropriate concentration slip.

If the multicomponent diffusion coefficients are retained without the binary assumption, the underlined terms in equation (D13) are to be replaced by

$$\left[ - \sum_{\substack{j=1 \\ j \neq i}}^{NS} \frac{N_{Le,ij}}{N_{Le}} \left( \frac{\partial C_j}{\partial \bar{n}} - C_j \sum_{q=1}^{NS} \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right) \right]_s$$

and the underlined terms in equation (D14) are to be replaced by

$$\left[ - \sum_{\substack{j=1 \\ j \neq i}}^{NS} \frac{N_{Le,ij}}{N_{Le}} \left( \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial C_j}{\partial \bar{s}} - C_j \sum_{q=1}^{NS} \frac{\bar{W}}{W_q} \frac{1}{1 + \bar{n}\bar{\kappa}} \frac{\partial C_q}{\partial \bar{s}} \right) \right]_s$$

where the multicomponent Lewis number  $N_{Le,ij}$  is defined as

$$N_{Le,ij} = \frac{\rho c_p D_{ij}}{K}$$

### Simplifications for a Binary Mixture

When all the species in a gas mixture can be considered as atoms and molecules only (ref. 9), equations (D11) through (D18) may be further simplified. With the assumption of  $P_y/p^s \approx 1$ , equations (D11) through (D18) for a binary mixture yield

Concentration slip:

$$\frac{C_A^s}{C_A^w} = \frac{\bar{\rho}_w}{\bar{\rho}_s} \frac{2 - \gamma_A}{2} \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} \quad (D22)$$

Pressure slip:

$$\begin{aligned} \bar{p}_s = \bar{p}_w + \frac{4}{5\sqrt{2\pi}} \left( \frac{\bar{\gamma}}{\bar{\gamma} - 1} \right)_s \frac{2 - \theta}{\theta} \frac{\varepsilon^2}{N_{Pr}} \frac{1}{\bar{T}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \\ \times \left( \frac{\bar{W}_s}{W_A} \right)^{3/2} \left[ C_A^s \bar{\mu}_A^s + \left( \frac{W_A}{W_M} \right)^{3/2} (1 - C_A^s) \bar{\mu}_M^s \right] \end{aligned} \quad (D23)$$

where we have used the following equation of state

$$\frac{\bar{p}_s}{\bar{\rho}_s} = \frac{1}{M_\infty^2} \frac{\bar{T}_s T_{ref}}{\bar{\gamma}_\infty T_\infty} \frac{\bar{W}_\infty}{\bar{W}_s} \quad (D24)$$

and neglected the higher order shear terms as well as diffusion terms.

Velocity slip:

$$\bar{u}_s = \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \varepsilon^2 \frac{\bar{\mu}_s}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \sqrt{\frac{\bar{W}_\infty}{\bar{W}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1 + \bar{n} \bar{\kappa}} \right)_s \quad (\text{D25})$$

where we have again employed the equation of state (eq. (D24)) and neglected higher order shear, conduction, and diffusion terms. In obtaining equation (D25), we have also used the following approximation:

$$\chi = \frac{[C_A^s(W_M - W_A) + W_A]^{1/2}}{C_A^s(\sqrt{W_M} - \sqrt{W_A}) + \sqrt{W_A}} \approx 1$$

For the equation to be more exact, one may keep this factor in equation (D25).

Temperature slip:

$$\bar{T}_s = \left[ \bar{T}_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} \chi_1 \left( \frac{\bar{\gamma}}{\bar{\gamma} - 1} \right)_s \frac{2-\theta}{\theta} \frac{\varepsilon^2}{(N_{Pr})_s} \frac{\bar{\mu}_s}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \right] / \left[ 1 - \frac{1}{4} \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \chi_1 \frac{\bar{\rho}_w \bar{k}_{wA}}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \frac{C_A^w}{C_A^s + 1} \right] \quad (\text{D26})$$

where

$$\chi_1 = \frac{[C_A(W_M - W_A) + W_A]^{3/2}}{C_A(W_M^{3/2} - 2W_A^{3/2}) + 2W_A^{3/2}}$$

and  $\frac{1}{2} \leq \chi_1 \leq 1$  for  $0 \leq C_A \leq 1$  and diatomic molecules ( $W_M = 2W_A$ ). In obtaining equation (D26), we have employed the equation of state (eq. (D24)) and  $W_M = 2W_A$ .

With frozen internal energy during reflection from the surface, the temperature slip equation becomes

$$\bar{T}_s = \left[ \bar{T}_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} \chi_2 \left( \frac{\bar{\gamma}}{\bar{\gamma} - 1} \right)_s \frac{2-\theta}{\theta} \frac{\varepsilon^2}{(N_{Pr})_s} \frac{\bar{\mu}_s}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s + \sqrt{\frac{\pi}{2}} \chi_2 \frac{\bar{\rho}_w \bar{k}_{wA}}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \left( \frac{C_A^w}{C_A^s + 1} \right) \bar{T}_w \right] / \left( 1 - \frac{5}{4} \sqrt{\frac{\pi}{2}} \chi_2 \frac{2-\theta}{\theta} \frac{\bar{k}_{wA} \bar{\rho}_w}{\sqrt{\bar{\rho}_s \bar{\rho}_s}} \frac{C_A^w}{C_A^s + 1} \right) \quad (\text{D27})$$

where

$$\chi_2 = \frac{[C_A(W_M - W_A) + W_A]^{3/2}}{C_A(W_M^{3/2} - W_A^{3/2}) + W_A^{3/2}}$$

For diatomic molecules ( $W_M = 2W_A$ ),  $\chi_2$  may be taken as unity for  $0 \leq C_A \leq 1$ . Equation (D27) employs  $W_M = 2W_A$ .

Equation for  $C_A^s$ :

$$C_A^s = \frac{2-\gamma_A}{2} \frac{\varepsilon^2}{\bar{k}_{wA}} \left( \frac{N_{Le}}{N_{Pr}} \right)_s \left( \frac{\bar{\mu}}{\bar{\rho}} \right)_s \sqrt{\frac{T_w}{\bar{T}_s T_{\text{ref}}}} \left( \frac{\partial C_A}{\partial \bar{n}} \right)_s \quad (\text{D28})$$

Equation (D28), for a noncatalytic surface with  $\gamma_A = \bar{k}_{wA} = 0$ , gives

$$\left(\frac{\partial C_A}{\partial \bar{n}}\right)_s = 0 \quad (\text{D29})$$

whereas using  $\gamma_A = 1$  in equation (D28) and in the expression for  $\bar{k}_{wA}$ ,

$$\bar{k}_{wA} = \frac{\gamma_A}{M_\infty} \sqrt{\frac{\bar{W}_\infty T_w}{2\pi\bar{\gamma}_\infty W_A T_\infty}} \quad (\text{D30})$$

would yield the appropriate concentration slip for a fully catalytic surface.

With the following (somewhat inconsistent) assumptions, equations (D23), (D25), (D27), and (D28) may be simplified to those obtained in reference 9 and employed in reference 12:

(i) In pressure slip equation (D23),  $N_{Pr} = 1$  is employed along with approximations

$$\frac{4}{5} \left(\frac{\bar{\gamma}}{\bar{\gamma} - 1}\right)_s \approx 3$$

and

$$\left(\frac{\bar{W}_s}{W_A}\right)^{3/2} \left[ C_A^s \bar{\mu}_A^s + \left(\frac{W_A}{W_M}\right)^{3/2} (1 - C_A^s) \bar{\mu}_M^s \right] \approx \bar{\mu}_s$$

(ii) In velocity slip equation (D25), the following assumption is made for the mixture molecular weights

$$\frac{\bar{W}_\infty}{\bar{W}_s} \approx 1$$

(iii) In temperature slip equation (D27), an assumption is made that the surface is noncatalytic so that  $\bar{k}_{wA} = 0$ . In addition, Prandtl number  $N_{Pr}$  is taken as unity, and it is assumed that

$$\frac{1}{2} \left(\frac{\bar{\gamma}}{\bar{\gamma} - 1}\right)_s \approx \frac{15}{8}$$

(iv) No assumption is required in the concentration slip equation (D28). But it may not be appropriate to employ (ref. 12) this equation for all the species of a multicomponent mixture. This equation is applicable to concentration slip of recombining atoms only in a binary (two-species) mixture (ref. 9) of atoms and molecules.

No equation has been obtained in reference 9 or 12 to correspond to equation (D22) to obtain wall values of the species concentration ( $C_A^w$ ) from the values at the edge of the Knudsen layer ( $C_A^s$ ).

### Slip Expressions For Single-Species Gas

For a single-species gas ( $\gamma_A = 0$ ), the following slip expressions are obtained:

Density slip:

$$\frac{\bar{\rho}_s}{\bar{\rho}_w} = \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} \quad (\text{D31})$$

Pressure slip:

$$\bar{p}_s = \bar{p}_w + \frac{4}{5\sqrt{2\pi}} \left(\frac{\bar{\gamma}}{\bar{\gamma} - 1}\right)_s \frac{2 - \theta}{\theta} \frac{\varepsilon^2}{(N_{Pr})_s} \frac{\bar{\mu}_s}{\bar{T}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left(\frac{\partial \bar{T}}{\partial \bar{n}}\right)_s \quad (\text{D32})$$

Velocity slip:

$$\bar{u}_s = \sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \varepsilon^2 \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1 + \bar{n} \bar{\kappa}} \right)_s \quad (\text{D33})$$

Temperature slip (for a gas consisting of molecules only (i.e., diatomic perfect gas)):

$$\bar{T}_s = \bar{T}_w + \frac{1}{4} \sqrt{\frac{\pi}{2}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{2-\theta}{\theta} \frac{\varepsilon^2}{(NPr)_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (\bar{\gamma}_s = 9/7) \quad (\text{D34a})$$

where we have used  $\chi_1 = \frac{1}{2}$  and assumed that the diatomic molecules possess full rotational as well as vibrational degrees of freedom at the edge of the Knudsen layer, implying  $\bar{\gamma}_s = 9/7$ . Generally this would be true due to the high temperatures at the Knudsen layer edge. However, for perfect air,  $\bar{\gamma}_\infty$  is generally taken as 7/5 with the excitation of only the rotational degree of freedom. For such an analysis, therefore,  $\bar{\gamma}_s$  would also be equal to 7/5. In this case (with only the rotational degree of freedom excited), equation (D34a) would be modified to

$$\bar{T}_s = \bar{T}_w + \frac{1}{3} \sqrt{\frac{\pi}{2}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{2-\theta}{\theta} \frac{\varepsilon^2}{(NPr)_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (\bar{\gamma}_s = 7/5) \quad (\text{D34b})$$

With frozen internal energy during reflection from the surface or for a monoatomic gas, we obtain

$$\bar{T}_s = \bar{T}_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{2-\theta}{\theta} \frac{\varepsilon^2}{(NPr)_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (\text{D35})$$

where  $\bar{\gamma}_s = 7/5$  for perfect air, and  $\gamma_s = 5/3$  for a monoatomic gas. Equations (D32), (D33), and (D35) are the ones employed in references 9 and 12 with  $NPr = 1$ .

### No-Slip Species Concentration Boundary Condition

**Multicomponent mixture.** The no-slip boundary condition may be obtained from equations (D17) and (D18). In the absence of slip, the thickness of the Knudsen layer shrinks to almost zero, and the values at the top of the Knudsen layer become the wall values (see fig. 1):

$$C_i^w = 1 + \left( \frac{\partial C_i}{\partial \bar{n}} + \frac{W_A}{W_i} \bar{\psi}_i \right)_w \bigg/ \sum_{q=1}^{\text{NS}} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_w \quad \begin{cases} (A = \text{O for } M = \text{O}_2) \\ (A = \text{N for } M = \text{N}_2) \end{cases} \quad (\text{D36})$$

where

$$\bar{\psi}_A^w = -\frac{2\gamma_A}{2-\gamma_A} \frac{1}{\varepsilon^2 M_\infty} \sqrt{\frac{\bar{W}_\infty T_w}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \frac{\bar{W}_w}{W_A} \left( \frac{NPr}{NLe} \right)_w \left( \frac{\bar{\rho}}{\bar{\mu}} \right)_w C_A^w \quad (A = \text{O, N}) \quad (\text{D37a})$$

$$\bar{\psi}_M^w = -\bar{\psi}_A^w \quad \begin{cases} (A = \text{O for } M = \text{O}_2) \\ (A = \text{N for } M = \text{N}_2) \end{cases} \quad (\text{D37b})$$

$$\bar{\psi}_i = 0 \quad (\text{For all other species}) \quad (\text{D37c})$$

and we have neglected the higher order shear (i.e.,  $P_y/p^w \approx 1$ ).

For the recombining O and N atoms, equation (D17) may also be written as

$$C_A^w = \left( \frac{\partial C_A}{\partial \bar{n}} + \sum_{q=1}^{\text{NS}} \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_w \bigg/ \left[ \sum_{q=1}^{\text{NS}} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_w + \frac{\bar{k}_{wA} \bar{W}_w}{\varepsilon^2 W_A} \left( \frac{NPr}{NLe} \right)_w \left( \frac{\bar{\rho}}{\bar{\mu}} \right)_w \right] \quad (\text{D38})$$

The recombination rate constant  $\bar{k}_{wA}$  in equations (D37a) and (D38) has been defined as (ref. 2)

$$\bar{k}_{wA} = \frac{2\gamma_A}{2 - \gamma_A} \frac{1}{M_\infty} \sqrt{\frac{\bar{W}_\infty T_w}{2\pi\bar{\gamma}_\infty W_A T_\infty}} \quad (\text{D39})$$

without slip and higher order shear.

For a noncatalytic wall (with  $\gamma_A = \bar{k}_{wA} = 0$ ), equation (D21) gives

$$\left(\frac{\partial C_i}{\partial \bar{n}}\right)_w = 0 \quad (\text{D40})$$

for all the species of a multicomponent mixture with the binary assumption about the diffusion coefficients.

**Binary mixture.** For a two-species mixture of atoms and molecules, equation (D28) gives

$$C_A^w = \frac{\varepsilon^2}{\bar{k}_{wA}} \left(\frac{N_{Le}}{N_{Pr}}\right)_w \left(\frac{\bar{\mu}}{\bar{\rho}}\right)_w \left(\frac{\partial C_A}{\partial \bar{n}}\right)_w \quad (\text{D41})$$

which may also be obtained from equation (D38) for a surface with finite catalyticity. In equation (D41),  $\bar{k}_{wA}$  is again obtained from equation (D39). For a noncatalytic surface with  $\bar{k}_{wA} = 0$ , equation (D41) gives

$$\left(\frac{\partial C_A}{\partial \bar{n}}\right)_w = 0 \quad (\text{D42})$$

Equations (D41) and (D42) are obtained in reference 4. However, in reference 4, equation (D30) is employed in place of equation (D39) for obtaining the reaction rate constant  $\bar{k}_{wA}$ . As obtained in reference 2, equation (D30) is more appropriate when slip and higher order shear are included in the flow-field analysis (e.g., under rarefied or low density conditions).

If  $\bar{k}_{wA}$  is substituted from equation (D39) into equation (D41), we may also obtain

$$C_A^w = \varepsilon^2 \frac{2 - \gamma_A}{\gamma_A} \left(\frac{N_{Le}}{N_{Pr}}\right)_w \sqrt{\frac{\pi W_A \bar{\mu}_w}{2 \bar{W}_w \bar{\rho}_w}} \sqrt{\frac{\bar{p}_w}{\bar{\rho}_w}} \left(\frac{\partial C_A}{\partial \bar{n}}\right)_w \quad (\text{D43})$$

where we have used the following equation of state:

$$\frac{\bar{p}_w}{\bar{\rho}_w} = \frac{1}{M_\infty^2} \frac{T_w}{\bar{\gamma}_\infty T_\infty} \frac{\bar{W}_\infty}{\bar{W}_w} \quad (\text{D44})$$

Equation (D43) compares with the corresponding equation of reference 9, if one keeps in mind that the diffusion coefficient  $F_D$  (of ref. 9) in the absence of slip is related to the present variables by the relation

$$F_D^w = \bar{\mu}_w \left(\frac{N_{Le}}{N_{Pr}}\right)_w$$

It may be seen from equation (D41) or (D43) that the gradient  $(\partial C_A / \partial \bar{n})_w$  is governed by the ratio  $\bar{k}_{wA} / \varepsilon^2$  or  $\gamma_A / \varepsilon^2$ . For surfaces which are almost noncatalytic, this ratio would be of the order of 1 for large values of the Reynolds number parameter  $(1/\varepsilon^2)$ . This would imply that  $(\partial C_A / \partial \bar{n})_w$  is not necessarily zero for such a surface if  $\varepsilon^2 \approx 0$ . In addition, equations (D41) and (D43) also imply that regardless of the surface catalytic activity, the higher density conditions (smaller values of  $\varepsilon^2$ ) would promote larger values of the concentration gradient at the surface.



By using the relations given by equation (E2) in equations (D11) through (D19), we can obtain the slip equations in the spherical polar coordinates for a multicomponent mixture. Once again, these equations employ the simplifications given in the section "Simplifications for Multicomponent Mixture" in the main text.

Concentration slip:

$$\frac{C_i^s}{C_i^w} = 2 \frac{\bar{\rho}_w}{\bar{\rho}_s} \left( 1 + \frac{1}{2} M_\infty \bar{M}_{iy} \sqrt{2\pi \bar{\gamma}_\infty \frac{W_i}{\bar{W}_\infty} \frac{T_\infty}{T_w}} \right) \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} / \left( \frac{P_y}{p^s} + 1 \right) \quad (\text{E3})$$

where

$$\bar{M}_{Ay} = -\bar{k}_{wA} \quad (A = \text{O}, \text{N}) \quad (\text{E4a})$$

$$\bar{M}_{My} = \bar{k}_{wA} \left( \frac{C_A}{C_M} \right)_w \quad \left( \begin{array}{l} A = \text{O for } M = \text{O}_2 \\ A = \text{N for } M = \text{N}_2 \end{array} \right) \quad (\text{E4b})$$

$$\bar{M}_{iy} = 0 \quad (\text{For all other atoms and molecules}) \quad (\text{E4c})$$

Pressure slip:

$$\begin{aligned} \bar{p}_s = & \left\{ \bar{p}_w - \varepsilon^2 \left[ \frac{2}{3} \bar{\mu} \left( \frac{1}{\bar{r}} \frac{\partial \bar{u}}{\partial \phi} - 2 \frac{\partial \bar{v}}{\partial \bar{r}} \right) \right]_s \right. \\ & + \varepsilon^2 \left[ \frac{2}{5\sqrt{\pi}} \frac{2-\theta}{\theta} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{1}{M_\infty (N_{Pr})_s} \sqrt{\frac{2T_{\text{ref}} \bar{T}_s \bar{W}_\infty}{\bar{\gamma}_\infty T_\infty \bar{W}_s}} \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{r}} \right)_s \right. \\ & \times \left. \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \bar{\mu}_i^s \right] \left. \right\} / \left\{ 1 - \frac{4}{\sqrt{\pi}} \frac{2-\theta}{\theta} \varepsilon^2 M_\infty \frac{(N_{Le})_s}{(N_{Pr})_s} \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2T_{\text{ref}} \bar{T}_s}} \frac{\bar{\mu}_s}{\bar{\rho}_s} \right. \\ & \times \left. \sum_{i=1}^{\text{NS}} \sqrt{\frac{W_i}{W_\infty}} \left[ \frac{\partial C_i}{\partial \bar{r}} + (1 - C_i) \sum_{q=1}^{\text{NS}} \frac{W}{W_q} \frac{\partial C_q}{\partial \bar{r}} \right]_s \right\} \quad (\text{E5}) \end{aligned}$$

Velocity slip:

$$\begin{aligned} \bar{u}_s = & \varepsilon^2 \frac{M_\infty \bar{\mu}_s}{\bar{\rho}_s} \left( 1 / \sum_{i=1}^{\text{NS}} \sqrt{\frac{\bar{W}}{W_i}} C_i \right)_s \left\{ \sqrt{\pi} \frac{2-\theta}{\theta} \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2T_{\text{ref}} \bar{T}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{r}} - \frac{\bar{u}}{\bar{r}} \right. \right. \\ & + \left. \left. \frac{1}{\bar{r}} \frac{\partial \bar{v}}{\partial \phi} \right)_s + \frac{1}{5} \frac{1}{M_\infty (N_{Pr})_s} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{r}} \right)_s \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \frac{\bar{\mu}_i^s}{\bar{\mu}_s} \right. \\ & + \left. \frac{(N_{Le})_s}{M_\infty (N_{Pr})_s} \sum_{i=1}^{\text{NS}} \sqrt{\frac{W_i}{\bar{W}_s}} \left[ \frac{\partial C_i}{\partial \bar{r}} + (1 - C_i) \sum_{q=1}^{\text{NS}} \frac{W}{W_q} \frac{\partial C_q}{\partial \bar{r}} \right]_s \right\} \quad (\text{E6}) \end{aligned}$$

Temperature slip:

$$\begin{aligned}
\frac{\bar{T}_s}{\bar{T}_w} = & \left\{ -\sqrt{\frac{\pi}{2}} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} + \sum_i \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right) \right. \\
& \left. + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \left[ \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s + \sum_i \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] \right\} / \left\{ -\sqrt{\frac{\pi}{2}} \right. \\
& \times \frac{2-\theta}{\theta} \left[ \frac{\varepsilon^2}{2\bar{\gamma}_\infty} \frac{1}{M_\infty^2 (NPr)_s} \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{T_{\text{ref}}}{T_\infty} \sqrt{\frac{\bar{\rho}_s}{\bar{p}_s}} \frac{\bar{W}_\infty}{\bar{W}_s} \left( \frac{\partial T}{\partial \bar{r}} \right)_s \right. \\
& \left. - \frac{5}{4} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} - \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_i \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right] \\
& \left. + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \sum_i \left( \frac{W_s}{W_i} \right)^{3/2} C_i^s \right\} \quad (\text{E7})
\end{aligned}$$

or, with frozen internal energy during reflection from surface,

$$\begin{aligned}
\frac{\bar{T}_s}{\bar{T}_w} = & \left[ -\sqrt{\frac{\pi}{2}} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} + \frac{1}{2} \left( \frac{P_y}{p^s} + 1 \right) \right. \\
& \left. \times \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] / \left\{ -\sqrt{\frac{\pi}{2}} \frac{2-\theta}{\theta} \left[ \frac{\varepsilon^2}{2\bar{\gamma}_\infty} \frac{1}{M_\infty^2 (NPr)_s} \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \frac{T_{\text{ref}}}{T_\infty} \right. \right. \\
& \left. \left. \times \sqrt{\frac{\bar{\rho}_s}{\bar{p}_s}} \frac{\bar{W}_\infty}{\bar{W}_s} \left( \frac{\partial T}{\partial \bar{r}} \right)_s - \frac{5}{4} \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \sum_{i=1}^{\text{NS}} \bar{M}_{iy} C_i^w \frac{\bar{W}_s}{W_i} \right] + \frac{1}{4} \left( 3 \frac{P_y}{p^s} + 1 \right) \right. \\
& \left. \times \sum_{i=1}^{\text{NS}} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right\} \quad (\text{E8})
\end{aligned}$$

$$C_i^s = 1 + \left( \frac{\partial C_i}{\partial \bar{r}} + \frac{W_A}{W_i} \bar{\psi}_i \right)_s / \sum_{q=1}^{\text{NS}} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{r}} \right)_s \quad \left( \begin{array}{l} A = \text{O for } i = \text{O}_2 \\ A = \text{N for } i = \text{N}_2 \end{array} \right) \quad (\text{E9})$$

where

$$\bar{\psi}_A^s = -\frac{\gamma_A}{2-\gamma_A} \frac{1}{\varepsilon^2 M_\infty} \sqrt{\frac{\bar{W}_\infty T_s}{2\pi\bar{\gamma}_\infty W_A T_\infty} \frac{\bar{W}_s}{W_A}} \times \left(\frac{N_{Pr}}{N_{Le}}\right)_s \left(\frac{\bar{\rho}}{\bar{\mu}}\right)_s \left(\frac{P_y}{p^s} + 1\right) C_A^s \quad (A = O, N) \quad (\text{E10a})$$

$$\bar{\psi}_M^s = -\bar{\psi}_A^s \quad \begin{pmatrix} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{pmatrix} \quad (\text{E10b})$$

$$\bar{\psi}_i^s = 0 \quad (\text{For all other species}) \quad (\text{E10c})$$

and

$$\frac{P_y}{p_s} = \frac{\bar{P}_y}{\bar{p}_s} = 1 + \frac{2\bar{\gamma}_\infty T_\infty}{3 T_{\text{ref}}} \left(\frac{\bar{\mu}}{\bar{\rho T}}\right)_s \frac{\bar{W}_s}{\bar{W}_\infty} \varepsilon^2 M_\infty^2 \left(\frac{\partial \bar{u}}{\partial \bar{r}} - 2 \frac{\partial \bar{v}}{\partial \bar{r}}\right)_s \quad (\text{E11})$$

In obtaining these various equations, the following form of the equation of state has been employed:

$$\frac{\bar{p}_s}{\bar{\rho}^s} = \frac{1}{M_\infty^2} \frac{\bar{T}_s T_{\text{ref}} \bar{W}_\infty}{\bar{\gamma}_\infty T_\infty \bar{W}_s} \quad (\text{E12})$$

Similar to Appendix D, equations (E3) through (E11) may further be simplified for a binary mixture and for a single-species gas.

## Appendix F

### Integrals Required for Obtaining Various Fluxes

In order to obtain the normal fluxes of mass, momentum, and energy, it is necessary to evaluate various integrals over the velocity space of the distribution function. These integrals involve terms that are various velocity moments of the distribution function. The integrals are provided for the net, incident, and specularly reflected fluxes. These integrals are basically the same as those provided in reference 2 except for some corrections and additions.

#### Integrals Over Entire Velocity Space (for Net Quantities)

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{1}{2} \pi^{3/2} \quad (i = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W^2 \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{5}{4} \pi^{3/2} \quad (i = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i^2 \exp(-W^2) d^3W = \frac{1}{4} \pi^{3/2} \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^4 \exp(-W^2) d^3W = \frac{3}{4} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j^2 \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W^2 \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j W^2 \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W^4 \exp(-W^2) d^3W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W^4 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{35}{8} \pi^{3/2} \quad (i = y)$$

### Integrals Over Lower Half of Velocity Space (for Incident Quantities)

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y \exp(-W^2) d^3W = -\frac{\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{1}{4} \pi^{3/2} \quad (i = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W^2 \exp(-W^2) d^3W = -\pi$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j)$$

$$= -\frac{\pi}{4} \quad (i = j \neq y)$$

$$= -\frac{\pi}{2} \quad (i = j = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_{\parallel} W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j; i \text{ or } j \neq \parallel)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{5}{8} \pi^{3/2} \quad (i = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y^2 W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j; i \text{ or } j \neq y)$$

$$= \frac{1}{8} \pi^{3/2} \quad (i = j \neq y)$$

$$= \frac{3}{8} \pi^{3/2} \quad (i = j = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y^2 W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= -\frac{3}{2} \pi \quad (i = y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_{\parallel} W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq \parallel \neq y)$$

$$= -\frac{3\pi}{4} \quad (i = \parallel \neq y)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W^4 \exp(-W^2) d^3W = -3\pi$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i W^4 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$= \frac{35}{16} \pi^{3/2} \quad (i = y)$$

**Integrals Over Upper Half of Velocity Space (for Specularly Reflected Quantities)**

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y \exp(-W^2) d^3W = \frac{\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) \exp(-W^2) d^3W = -\frac{1}{4} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W^2 \exp(-W^2) d^3W = \pi$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j)$$

$$= \frac{\pi}{4} \quad (i = j \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y)^2 \exp(-W^2) d^3W = \frac{\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_{\parallel} W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j; i \text{ or } j \neq \parallel)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W^2 \exp(-W^2) d^3W = -\frac{5}{8} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j \exp(-W^2) d^3W = 0 \quad (i \neq j; i \text{ or } j \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W_i^2 \exp(-W^2) d^3W = -\frac{1}{8} \pi^{3/2} \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 (-W_y)^2 \exp(-W^2) d^3W = \frac{3}{8} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y)^2 W^2 \exp(-W^2) d^3W = \frac{3\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_{\parallel} W_i W^2 \exp(-W^2) d^3W = 0 \quad (i \neq \parallel \neq y)$$

$$= \frac{3\pi}{4} \quad (i = \parallel \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W^4 \exp(-W^2) d^3W = 3\pi$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W^4 \exp(-W^2) d^3W = 0 \quad (i \neq y)$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W^4 \exp(-W^2) d^3W = -\frac{35}{16} \pi^{3/2}$$

The term  $(-W_y)$  appearing in the integrals emphasizes that the sign of the thermal velocity component normal to the surface  $V_y$  (and consequently that of  $W_y$ ) changes in the distribution function  $f_s^\downarrow$  upon reflection from the surface. This implies that the distribution function  $f_s^\uparrow(V_x, V_y, V_z) = f_s^\downarrow(V_x, -V_y, V_z)$ .

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16. Abstract Equations are presented for the surface-slip (or jump) values of species concentration, pressure, velocity, and temperature in the low Reynolds number, high-altitude flight regime of a space vehicle. These are obtained from closed-form solutions of the mass, momentum, and energy flux equations by using the Chapman-Enskog velocity distribution function. This function represents a solution of the Boltzmann equation in the Navier-Stokes approximation. The analysis, obtained for nonequilibrium multicomponent airflow, includes the finite-rate surface catalytic recombination and changes in the internal energy during reflection from the surface. Expressions for the various slip quantities have been obtained in a form which can readily be employed in flow-field computations. A consistent set of equations is provided for multicomponent and binary mixtures and single-species gas. An expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture in the absence of slip.			
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